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I. DERIVATIVES OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.[1]

BY J. MERRITT MATTHEWS.

Received September 2, 1898.

1. INTRODUCTION.

THE tetrachlorides of several of the members of Group IV have been studied in their deportment with certain organic nitriles and amines, and the results seem to indicate that there is a general tendency toward reactions between these tetrachlorides and the latter-named reagents, giving rise to definitely constituted compounds. That is to say, the tetrachlorides of Group IV appear to possess an acidic character in their ability to combine with certain organic bases to form neutral salts. This behavior has already been studied with reference to the tetrachlorides of carbon, silicon, titanium, and tin; and although the data at our command are neither as connected nor as complete as might be desired, nevertheless, they may be regarded as sufficient to establish a characteristic group reaction. In these reactions, however, there appear to be several unaccountable fluctuations and divergences among the different members of the group. It would be natural to expect a difference in the behavior of the metallic subgroup including germanium, tin, and lead, from the more non-metallic subgroup including titanium, zirconium, and thorium. But such a conclusion does not

[1] From author's thesis for the Degree of Doctor of Philosophy.

appear to receive the necessary strength from the actual facts observed in order to give it a sure foundation; for titanium seems to exhibit a greater analogy in its reactions to those of tin than to any other. The number of reactions studied, however, have been so few that it would be presumptuous to formulate a comprehensive law regarding the general reactions of the two subgroups in question, and in consequence of there being no such law established, it would be illogical to argue that apparently diverging reactions pointed necessarily to inconsistencies in the behavior of the two subgroups.

The tetrachlorides of silicon, titanium, and tin have been rather comprehensively studied in their behavior toward nitriles and amines. Titanium tetrachloride has been found to be reactive with formonitrile, acetonitrile, benzonitrile, toluonitrile, succinonitrile, chlorcyanogen, sulphur monochloride, phosphorus pentachloride, and the vapors of aqua regia. The tetrachloride of tin also exhibits analogous reactions with every one of the above-mentioned reagents; silicon tetrachloride, however, shows no evidence of reacting with these compounds.

All three of these tetrachlorides give derivatives with ammonia and aromatic amines, as does also carbon tetrachloride. With the fatty amines, however, only the chlorides of silicon and tin have been found to be reactive.

2. PREPARATION OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.

A. ZIRCONIUM TETRACHLORIDE.

The zirconium tetrachloride used in this research was prepared in the following manner: Carefully selected crystals of zircon were finely powdered and fused with acid potassium sulphate; the fusion was lixiviated with water, and filtered; the residue was dried and fused with potassium hydroxide in a nickel dish. This fusion, after being digested with water, and filtered, left a white amorphous residue of zirconium dioxide. The oxide was mixed with pulverized starch and molasses to a thick batter, which was then rolled into small pellets about one centimeter in diameter. These were slowly dried in an air oven until all moisture was expelled, when they were transferred to a covered silver crucible and charred until no more vapors were

evolved. These pellets, containing zirconium dioxide intimately mixed with pure charcoal, were placed in a long glass combustion tube, and strongly heated in a current of dry chlorine gas. Zirconium tetrachloride was formed by this procedure, and collected in the cooler part of the tube in the form of a white powder or minute crystals. The salt thus obtained was dissolved in ether which had been carefully dehydrated by repeated distillation over sodium, until thin slices of the metal remained untarnished on being in contact with the ether for several days. The zirconium tetrachloride in the form of this ethereal solution was used in all the experiments, as it gave a convenient and uniform method for testing the reactions.

B. THORIUM TETRACHLORIDE.

This salt was prepared in a manner precisely analogous to that given for zirconium. The dioxide, ThO_2, was obtained from a quantity of the nitrate which was available for the purpose, by precipitation with ammonium hydroxide and subsequent ignition. The tetrachloride was dissolved in dehydrated ether, as in the case of the zirconium salt, and this solution was used in all of the reactions.

C. LEAD TETRACHLORIDE.

This compound was prepared by the method of Friedrich.[1] One part of lead chloride was suspended in twenty parts of concentrated hydrochloric acid, and a current of chlorine gas was conducted through the liquid until nearly all of the lead dichloride had gone into solution, which required about twenty hours. The temperature of the liquid during the entire process was kept at about 4° C. by means of a freezing-mixture. The yellow-colored liquid which resulted from this treatment consisted of a solution of lead tetrachloride in concentrated hydrochloric acid. Two parts of ammonium chloride dissolved in ten parts of water were then added, and a bright lemon-yellow crystalline precipitate was produced, consisting of the ammonium double salt of lead tetrachloride, which, according to Friedrich, has the formula $PbCl_4.2NH_4Cl$. Classen and Zahorski,[2] however, apparently obtain the same salt—by practically the same

[1] *Ber. d. chem. Ges.*, 26, 1434.
[2] *Ztschr. anal. Chem.*, 4, 100.

method—and they ascribe to it the formula $2PbCl_4.5NH_4Cl$. The ammonium double salt was filtered off and washed free from hydrochloric acid and chlorine with absolute alcohol and ether. A portion of this salt was placed in a separatory funnel and digested with fuming sulphuric acid of specific gravity 1.879. A brisk reaction took place and yellow oily drops of lead tetrachloride soon separated out; these were washed by decantation several times with fuming sulphuric acid, and finally dissolved in chloroform which had been carefully dehydrated over fuming sulphuric acid. This chloroform solution of the lead tetrachloride was used for all the reactions; but fresh portions and solutions had to be made for each experiment, as the tetrachloride decomposed into the lower chloride in a few hours. It was found impossible to work with the liquid tetrachloride itself, as it was immediately decomposed on coming in contact with the air, and even decomposed in about twelve hours when kept under fuming sulphuric acid. The strength of the acid used for the decomposition of the ammonium double salt is an important factor in this preparation, as an acid of less strength than that used above will fail to give the lead tetrachloride in any appreciable quantity.

3. THE ACTION OF NITRILES, ETC., ON THE TETRACHLORIDES.

As zirconium occupies the next position to titanium in the same subgroup, it was natural to suppose that its tetrachloride would exhibit reactions with the nitriles somewhat analogous to those of the latter element, and that the analogy might also be followed into the fatty and aromatic amines. Contemporary with this present work there was carried to completion in this same laboratory a study of the reactions of silicon tetrachloride; and as both tin and titanium have been studied in this same connection, it was considered that a research into the possible derivatives of the allied members of this group might lead to results which would be useful in establishing analogies and comparisons between the different members of Group IV, as viewed from their respective behavior with the reagents used in this study. By this means it was thought probable that a definite law might be formulated for the group with regard to these

reactions, and that the heterogeneous data, heretofore lying dissociated and useless, might be brought together and systematically understood.

a. Vapors of Aqua Regia.—The dry vapors of aqua regia conducted into the solution of zirconium tetrachloride gave no reaction, the solution only becoming discolored by the gases, which were again liberated on raising the temperature. Portions of the dry zirconium salt were also placed in a porcelain boat, and heated in a current of the dry vapors of aqua regia; but the salt appeared to volatilize unchanged, and no compound was formed. In this behavior zirconium shows a deviation from that of titanium, as the tetrachloride of the latter reacts readily with the vapors of aqua regia, giving a compound corresponding to the formula $3TiCl_4.2NO_2Cl$, Hampe.[1] An analogous compound with tin tetrachloride has been prepared by the same investigator. Baeyer[2] also records the compound $SnCl_4.2NOCl$.

The solutions of the tetrachlorides of thorium and lead behaved similarly to that of zirconium, and gave no derivatives.

b. Nitrogen Dioxide.—This gas, obtained by heating lead nitrate, on being conducted into the solutions of the tetrachlorides, gave no reaction beyond a simple solution of the gas. The dry salts of zirconium and thorium, heated in a current of the gas, volatilized unchanged and gave no compound.

c. Sulphur Monochloride.—On mixing this substance with the solutions of the tetrachlorides, no reaction was observed.

d. Chlorides of Phosphorus.—The action of both the tri- and pentachlorides of phosphorus was tried on the solutions of the tetrachlorides, but no combination resulted.

e. Dicyanogen.—On conducting this gas into the solutions of the tetrachlorides, no reaction took place; nor does it seem to have formed any compounds with the corresponding salts of titanium or tin.

f. Formonitrile.—Though both titanium and tin tetrachlorides give derivatives with hydrocyanic acid, yet no product was obtained by allowing this compound to act on the three tetrachlorides here investigated.

g. Cyanogen Chloride.—It was prepared by the action of chlo-

[1] *Ann. Chem.* (Liebig), **126**, 43.
[2] *Ber. d. chem. Ges.*, **7**, 1639.

rine on mercuric cyanide, but it gave no reactions with the solutions of the tetrachlorides.

h. Acetonitrile.—The vapors of this nitrile passed into the solutions of the tetrachlorides yielded no compounds, although derivatives have been obtained with the titanium and tin salts.

i. Benzonitrile.—Like acetonitrile, this aromatic body yielded no derivatives with the tetrachlorides.

SUMMARY.

From these experiments it is to be observed that the nitriles and the other reagents here used, which for the most part gave additive compounds with the tetrachlorides of titanium and tin, are without action on the corresponding salts of zirconium, thorium, and lead.

4. ACTION OF FATTY AND AROMATIC AMINES.

It was in this field that positive results were at last encountered. Silicon, titanium, and tin tetrachlorides all give compounds with the amines, and analogy would lead us to expect that the chlorides here used would behave in a similar manner, as indeed was the case. These derivatives with the amine bases, including ammonia, are apparently peculiar additive products, showing that these tetrachlorides, in common with the other chlorides of this group, possess an acid character.

The compounds herein described were obtained by the simple addition of the pure anhydrous reagents to the solutions of the respective tetrachlorides. The zirconium and thorium derivatives, for the most part, were white flocculent precipitates; the lead salts, however, gave compounds of various colors.

The analysis of these derivatives was carried out in the following manner: With the zirconium and thorium compound a weighed quantity was placed in a small beaker-glass and covered with nitric acid containing a solution of silver nitrate, and gently warmed. This sufficed to decompose the substance, the chlorine present being precipitated as silver chloride. The liquid was diluted with water, the chloride filtered off, and from its weight the chlorine was estimated. Excess of ammonia water was added to the filtrate, and the resulting precipitate of zirconium or thorium hydroxide was filtered off and ignited to the corre-

sponding dioxide, from the weight of which the zirconium or thorium was estimated. The nitrogen present in the ammonia derivatives was determined by heating a portion with a strong solution of sodium hydroxide, and passing the evolved ammonia into a standardized solution of hydrochloric acid, and either titrating the excess of acid with standard alkali, or precipitating the ammonia in the usual manner with a solution of platinic chloride, and from the weight of the platinum left after ignition calculating the quantity of nitrogen. With the amine derivatives the Kjeldahl method was employed; and the Will and Varrentrap method was used for the quinoline and pyridine compounds. The lead compounds were decomposed with warm nitric acid, and the lead determined as sulphate by evaporation with sulphuric acid in the usual manner, the chlorine being determined by heating the compound with sulphuric acid in a distilling flask, passing the evolved hydrochloric acid gas into a solution of silver nitrate, and weighing the silver chloride as usual. The nitrogen present was estimated as with the zirconium and thorium derivatives.

A. AMMONIA.

Paykull[1] obtained a compound of zirconium tetrachloride with ammonia by heating the former with NH_4Cl, and to this compound he ascribes the formula $ZrCl_4.4NH_3$. Besson[2] has also obtained an ammonia derivative with silicon tetrachloride, giving it the formula $SiCl_4.6NH_3$. With tin tetrachloride Rose[3] obtained the compound $SnCl_4.4NH_3$, though Persoz[4] claims to have made $SnCl_4.6NH_3$. With titanium tetrachloride Rose[3] obtained the compound $TiCl_4.4NH_3$, though Persoz[5] gives the formula as $TiCl_4.6NH_3$.

a. Zirconium Tetrachloride, $ZrCl_4.8NH_3$. — On passing dry ammonia gas into the solution of zirconium tetrachloride, a white flocculent precipitate was immediately produced, with considerable evolution of heat. This compound on drying appeared to be stable in the air, though on gently heating it

[1] *Ber. d. chem. Ges.*, 6, 1467.
[2] *Compt. rend.*, 110, 240.
[3] Pogg. *Ann.*, 20, 147.
[4] *Ann. chim. phys.*, 46, 305.
[5] *Vide supra.*

gave off fumes of ammonium chloride. Its analysis showed the presence of eight molecules of ammonia.

I. 0.5625 gram material gave:

0.8729 gram silver chloride = 0.2161 gram chlorine = 38.42 per cent. chlorine.

0.1860 gram zirconium dioxide = 0.1374 gram zirconium = 24.44 per cent. zirconium.

II. 0.1862 gram material gave:

0.2881 gram silver chloride = 0.0713 gram chlorine = 38.30 per cent. chlorine.

0.0623 gram zirconium dioxide = 0.0460 gram zirconium = 24.71 per cent. zirconium.

0.0624 gram material gave 0.0228 gram ammonia = 36.60 per cent. ammonia.

0.5625 gram material gave 0.2084 gram ammonia = 37.05 per cent. ammonia.

	Calculated for $ZrCl_4.8NH_3$.	Found. I.	II.
Chlorine	38.52	38.42	38.30
Zirconium	23.58	24.44	24.71
Ammonia	36.90	36.60	37.05

$ZrCl_4.2NH_3$.—On passing dry ammonia gas over the solid zirconium tetrachloride contained in a porcelain boat, a considerable evolution of heat was observed, evidently showing that combination resulted. The compound thus obtained was white in color, fumed in the air, and rapidly took up moisture, rendering it difficult to analyze with accuracy.

0.5304 gram zirconium tetrachloride, after being treated with ammonia gas for two hours, on reweighing gave 0.6247 gram.

This on analysis gave:

1.3778 gram silver chloride = 0.3163 gram chlorine = 50.67 per cent. chlorine.

0.2927 gram zirconium dioxide = 0.2163 gram zirconium = 34.62 per cent. zirconium.

	Calculated for $ZrCl_4.2NH_3$.	Found.
Chlorine	51.81	50.67
Zirconium	33.21	34.26
	Gram.	Gram.
Increase in weight	0.0917	0.0943

$ZrCl_4.4NH_3$.—On heating zirconium tetrachloride in a current of dry ammonia gas, a compound was obtained which was white in color, and unstable on exposure to the air.

0.4713 gram zirconium tetrachloride being gently heated (to about 100° C.) in ammonia gas, on reweighing gave 0.6123 gram.

This on analysis gave:

1.1397 gram silver chloride = 0.2821 gram chlorine = 46.07 per cent. chlorine.

0.2588 gram zirconium dioxide = 0.1912 gram zirconium = 31.23 per cent. zirconium.

	Calculated for $ZrCl_4.4NH_3$.	Found.
Chlorine	47.24	46.07
Zirconium	30.14	31.23
	Gram.	Gram.
Increase in weight	0.1378	0.1410

These results seem to indicate that zirconium tetrachloride may be combined with ammonia in three proportions, depending upon the conditions under which the combination is brought about. When in ethereal solution it takes up eight molecules of ammonia, giving $ZrCl_4.8NH_3$; the dry salt unaided by heat gives $ZrCl_4.2NH_3$; and with the aid of heat the latter also gives the compound $ZrCl_4.4NH_3$. All of these bodies are white in color, the first one only being stable in the air. The last of the above derivatives seems to be identical with the one obtained by Paykull.

b. Thorium Tetrachloride.—As the field of thorium derivatives has not been investigated in any very exhaustive manner, one would not be likely to encounter any preceding research in the rather remote class of compounds herein dealt with. Chydenius,[1] however, has prepared a derivative of thorium tetrachloride with ammonium chloride, to which he has given the formula $ThCl_4.8NH_4Cl$. It is of interest to note that the compound prepared in this present research also contains the same molecular proportions of ammonia to thorium.

$ThCl_4.8NH_3$.—Dry ammonia gas passed into the solution of thorium tetrachloride produced a white flocculent precipitate, which, on drying, continued stable in the air. On heating, it

[1] *Jsb. Chem.*, *1863*, 194.

decomposed with the evolution of fumes of ammonium chloride.

I. 0.5870 gram material gave:

0.6526 gram silver chloride = 0.1616 gram chlorine = 27.52 per cent. chlorine.

0.3054 gram thorium dioxide = 0.2684 gram thorium = 45.73 per cent. thorium.

II. 0.6212 gram material gave:

0.5928 gram silver chloride = 0.1715 gram chlorine = 27.61 per cent. chlorine.

0.3212 gram thorium dioxide = 0.2824 gram thorium = 45.46 per cent. thorium.

0.5172 gram material gave 0.1366 gram ammonia = 26.41 per cent. ammonia.

	Calculated for $ThCl_4.8NH_3$.	Found. I.	II.
Chlorine	27.80	27.52	27.61
Thorium	45.55	45.73	45.46
Ammonia	26.64	26.41	....

$ThCl_4.6NH_3$.—On allowing dry ammonia gas to pass over a portion of thorium tetrachloride placed in a porcelain boat, a considerable evolution of heat was observed, the ammonia evidently reacting with the salt. The resulting compound was white in color, and fumed in moist air, though it appeared to be more stable than the corresponding zirconium derivative obtained under the same conditions.

0.4217 gram material, on being treated with ammonia gas for two hours, on reweighing gave 0.5352 gram. This on analysis gave:

0.6274 gram silver chloride = 0.1553 gram chlorine = 29.01 per cent. chlorine.

0.3021 gram thorium dioxide = 0.2656 gram thorium = 49.62 per cent. thorium.

	Calculated for $ThCl_4.6NH_3$.	Found.
Chlorine	29.79	29.01
Thorium	48.80	49.62
	Gram.	Gram.
Increase in weight	0.1148	0.1135

On gently heating thorium tetrachloride to about 100° C. in a current of ammonia gas, a compound was obtained identical

with the one just described above; it possessed the same appearance and analyzed for the same formula. At a higher temperature decomposition seemed to take place and copious fumes of ammonium chloride were formed.

c. Lead Tetrachloride, $PbCl_4.4NH_3$.—On treating the chloroform solution of lead tetrachloride with dry ammonia gas, an orange-yellow precipitate was at first produced, which rapidly became white in color as more ammonia was absorbed. A great amount of heat was evolved in the reaction, and the compound continued stable in the air.

I. 0.3600 gram material gave:

0.2597 gram lead sulphate = 0.1774 gram lead = 49.30 per cent. lead.

0.2614 gram material gave:

0.3205 gram silver chloride = 0.0816 gram chlorine = 33.76 per cent. chlorine.

II. 0.2582 gram material gave:

0.1874 gram lead sulphate = 0.1281 gram lead = 49.62 per cent. lead.

0.2075 gram material gave:

0.2844 gram silver chloride = 0.0704 gram chlorine = 33.92 per cent. chlorine.

0.4201 gram material gave:

0.3817 gram platinum = 0.0664 gram ammonia = 15.81 per cent. ammonia.

	Calculated for $PbCl_4.4NH_3$.	Found. I.	Found. II.
Lead	49.88	49.30	49.62
Chlorine	34.05	33.76	33.92
Ammonia	16.07	15.81	....

$PbCl_4.2NH_3$.—By using a more concentrated solution of lead tetrachloride, and interrupting the treatment with ammonia gas before all of the lead salt was neutralized, an orange-yellow precipitate was obtained. This fumed in the air and decomposed on standing. Its analysis indicated the above formula.

0.3017 gram material gave:

0.2375 gram lead sulphate = 0.1622 gram lead = 53.75 per cent. lead.

0.2332 gram material gave:

0.3525 gram silver chloride = 0.0873 gram chlorine = 37.42 per cent. chlorine.

0.2716 gram material gave:

0.1430 gram platinum = 0.0249 gram ammonia = 9.16 per cent. ammonia.

	Calculated for $PbCl_4.2NH_3$.	Found.
Lead	54.16	53.75
Chlorine	37.00	37.42
Ammonia	8.85	9.16

B. METHYLAMINE.

a. Zirconium Tetrachloride, $ZrCl_4.4CH_3NH_2$.—On conducting the vapors of methylamine into the solution of zirconium tetrachloride, a white flocculent precipitate was formed. Analysis showed that it followed the same general type as the other derivatives.

I. 0.2417 gram material gave:

0.3833 gram silver chloride = 0.0949 gram chlorine = 39.26 per cent. chlorine.

0.0838 gram zirconium dioxide = 0.0619 gram zirconium = 25.62 per cent. zirconium.

II. 0.5432 gram material gave:

0.8674 gram silver chloride = 0.2147 gram chlorine = 39.53 per cent. chlorine.

0.1786 gram zirconium dioxide = 0.1339 gram zirconium = 25.65 per cent. zirconium.

0.6021 gram material gave:

0.1165 gram ammonia = 0.0969 gram nitrogen = 15.95 per cent. nitrogen.

	Calculated for $ZrCl_4.4CH_3NH_2$.	Found. I.	Found. II.
Chlorine	39.82	39.36	39.53
Zirconium	25.41	25.62	25.65
Nitrogen	16.18	15.95	....

b. Thorium Tetrachloride, $ThCl_4.4CH_3NH_2$.—The compound obtained with thorium tetrachloride showed the presence of four molecules of the base. Indeed this seems to be the general type after which all these derivatives are modeled.

0.6513 gram material gave:

0.7451 gram silver chloride = 0.1802 gram chlorine = 28.32 per cent. chlorine.

0.3461 gram thorium dioxide = 0.3040 gram thorium = 46.71 per cent. thorium.

0.5318 gram material gave:

0.0712 gram ammonia = 0.0587 gram nitrogen = 11.03 per cent. nitrogen.

	Calculated for $ThCl_4.4CH_3NH_2$.	Found.
Chlorine	28.48	28.32
Thorium	46.65	46.71
Nitrogen	11.24	11.03

c. Lead Tetrachloride, $PbCl_4.4CH_3NH_2$.—The compound obtained with lead tetrachloride was also white in color, and stable in the air. Analysis proved it to be analogous to the preceding derivatives.

0.2506 gram material gave:

0.2969 gram silver chloride = 0.0735 gram chlorine = 29.32 per cent. chlorine.

0.2716 gram material gave:

0.1757 gram lead sulphate = 0.1200 gram lead = 44.17 per cent. lead.

0.2517 gram material gave:

0.2005 gram platinum = 0.0289 gram nitrogen = 11.42 per cent. nitrogen.

	Calculated for $PbCl_4.4CH_3NH_2$.	Found.
Chlorine	30.02	29.32
Lead	43.76	44.17
Nitrogen	11.84	11.42

C. ETHYLAMINE.

a. Zirconium Tetrachloride, $ZrCl_4.4C_2H_5NH_2$.—As would be expected from its behavior with the preceding amine, zirconium tetrachloride was found to yield a derivative with ethylamine.

0.5418 gram material gave:

0.7478 gram silver chloride = 0.1856 gram chlorine = 34.26 per cent. chlorine.

0.1619 gram zirconium dioxide = 0.1196 gram zirconium = 22.08 per cent. zirconium.

0.6516 gram material gave:

0.0861 gram ammonia = 0.0709 gram nitrogen = 10.89 per cent. nitrogen.

	Calculated for $ZrCl_4.4C_2H_5NH_2$.	Found.
Chlorine	34.42	34.26
Zirconium	21.96	22.08
Nitrogen	10.79	10.89

b. Thorium Tetrachloride, $ThCl_4.4C_2H_5NH_2$. — Ethylamine gave a white compound with thorium tetrachloride.

0.2102 gram material gave :

0.2137 gram silver chloride = 0.0528 gram chlorine = 25.12 per cent. chlorine.

0.0995 gram thorium dioxide = 0.0874 gram thorium = 41.58 per cent. thorium.

0.5912 gram material gave :

0.0712 gram ammonia = 0.0587 gram nitrogen = 9.92 per cent. nitrogen.

	Calculated for $ThCl_4.4C_2H_5NH_2$.	Found.
Chlorine	25.60	25.12
Thorium	41.94	41.58
Nitrogen	10.10	9.92

c. Lead Tetrachloride, $PbCl_4.4C_2H_5NH_2$.—Ethylamine gave at first a yellow precipitate with the solution of lead tetrachloride, which went over to a white compound on the addition of more ethylamine.

0.2072 gram material gave :

0.2220 gram silver chloride = 0.0550 gram chlorine = 25.52 per cent. chlorine.

0.2506 gram material gave :

0.1459 gram lead sulphate = 0.0996 gram lead = 39.76 per cent. lead.

0.3817 gram material gave :

0.2746 gram platinum = 0.0394 gram nitrogen = 10.32 per cent. nitrogen.

	Calculated for $PbCl_4.4C_2H_5NH_2$.	Found.
Chlorine	26.84	26.52
Lead	39.13	39.76
Nitrogen	10.59	10.32

D. PROPYLAMINE.

a. Zirconium Tetrachloride, $ZrCl_4.4C_3H_7NH_2$.—With propylamine, zirconium tetrachloride gave a white compound similar in appearance to the foregoing derivatives.

0.3390 gram material gave:

0.4112 gram silver chloride = 0.1020 gram chlorine = 30.10 per cent. chlorine.

0.0897 gram zirconium dioxide = 0.0663 gram zirconium = 19.55 per cent. zirconium.

0.6229 gram material gave:

0.0892 gram ammonia = 0.0736 gram nitrogen = 11.80 per cent. nitrogen.

	Calculated for $ZrCl_4.4C_3H_7NH_2$.	Found.
Chlorine	30.30	30.10
Zirconium	19.33	19.55
Nitrogen	11.96	11.80

b. Thorium Tetrachloride, $ThCl_4.4C_3H_7NH_2$. — Propylamine gave a white compound with thorium tetrachloride.

0.2682 gram material gave:

0.2537 gram silver chloride = 0.0628 gram chlorine = 23.40 per cent. chlorine.

0.1167 gram thorium dioxide = 0.1026 gram thorium = 38.22 per cent. thorium.

0.4213 gram material gave:

0.0460 gram ammonia = 0.0379 gram nitrogen = 9.01 per cent. nitrogen.

	Calculated for $ThCl_4.4C_3H_7NH_2$.	Found.
Chlorine	23.25	23.40
Thorium	38.09	38.22
Nitrogen	9.18	9.01

c. Lead Tetrachloride, $PbCl_4.4C_3H_7NH_2$.—Propylamine at first gave a dark reddish brown precipitate with lead tetrachloride soon becoming almost white in color, having a faint yellow tinge.

0.2507 gram material gave:

0.2065 gram silver chloride = 0.0511 gram chlorine = 20.39 per cent. chlorine.

0.2672 gram material gave:

0.1195 gram lead sulphate = 0.0817 gram lead = 30.56 per cent. lead.

0.2817 gram material gave:

0.1513 gram platinum = 0.0217 gram nitrogen = 7.82 per cent. nitrogen.

	Calculated for $PbCl_4.4C_3H_7NH_2$.	Found.
Chlorine	20.73	20.39
Lead	30.22	30.56
Nitrogen	8.28	7.82

E. ANILINE.

Schiff[1] has obtained a compound of tin tetrachloride with aniline, to which he has given the formula $SnCl_4.4C_6H_5NH_2$, while with titanium tetrachloride Leeds[2] describes a derivative having the formula $TiCl_4.4C_6H_5NH_2$.

In all of these derivatives the aniline appears to be merely additive. With silicon tetrachloride, however, aniline seems to form a substitution product corresponding to the formula $SiCl_2.(C_6H_5NH)_2$; Harden,[3] Reynolds,[4] and Harold.[5]

a. Zirconium Tetrachloride, $ZrCl_4.4C_6H_5NH_2$.—On the addition of aniline to the solution of zirconium tetrachloride a grayish flocculent precipitate was produced. This was carefully washed with anhydrous ether until all traces of aniline were removed. It appeared to be stable on drying, and its analysis showed the presence of four molecules of aniline.

I. 0.5382 gram material gave:

0.5053 gram silver chloride = 0.1251 gram chlorine = 23.25 per cent. chlorine.

0.1080 gram zirconium dioxide = 0.0798 gram zirconium = 14.83 per cent. zirconium.

II. 04817 gram material gave:

0.4538 gram silver chloride = 0.1123 gram chlorine = 23.32 per cent. chlorine.

0.0982 gram zirconium dioxide = 0.0726 gram zirconium = 15.06 per cent. zirconium.

I. 0.5382 gram material gave:

[1] *Jsb. Chem.*, *1863*, 412.
[2] This Journal, 3, 145.
[3] *J. Chem. Soc.*, 51, 40.
[4] *Ibid.*, 55, 474.
[5] *Thesis*, Univ. of Pennsylvania, *1897*.

0.0600 gram ammonia = 0.0494 gram nitrogen = 9.19 per cent. nitrogen.

II. 0.6108 gram material gave:

0.0678 gram ammonia = 0.0559 gram nitrogen = 9.15 per cent. nitrogen.

	Calculated for $ZrCl_4.4C_6H_5NH_2$.	Found. I.	II.
Chlorine	23.49	23.25	23.32
Zirconium	14.98	14.83	15.06
Nitrogen	9.27	9.19	9.15

Since analysis would show no difference in the composition of $ZrCl_4.4C_6H_5NH_2$ and a mixture of $ZrCl_2(C_6H_5NH)_2+2C_6H_5NH_2.HCl$, the following method was resorted to in order to prove that it was the first and not the second compound which was formed. The substance, after having been completely freed from aniline, was treated with chloroform, in which it proved to be easily and completely soluble, whereas aniline hydrochloride is insoluble in the same reagent, and hence was not present in the compound. Also no substituted chloraniline, $C_6H_4ClNH_2$, could have been formed, as this is soluble in ether, and the existence of no such substance was indicated in the ethereal filtrate. This conclusively proves that the compound is purely additive in nature, and has the formula $ZrCl_4.4C_6H_5NH_2$. This same proof may be used as an argument for the additive character of all the zirconium and thorium derivatives described in this research.

b. Thorium Tetrachloride, $ThCl_4.4C_6H_5NH_2$. — Aniline produced a precipitate slightly gray in color, and soluble in chloroform. Its analysis indicated a formula in correspondence with that of the zirconium derivative.

0.2536 gram material gave:

0.1940 gram silver chloride = 0.0479 gram chlorine = 18.89 per cent. chlorine.

0.0906 gram thorium dioxide = 0.0796 gram thorium = 31.39 per cent. thorium.

0.5536 gram material gave:

0.0488 gram ammonia = 0.0402 gram nitrogen = 7.41 per cent. nitrogen.

	Calculated for $ThCl_4.4C_6H_5NH_2$.	Found.
Chlorine	19.02	18.89
Thorium	31.15	31.39
Nitrogen	7.61	7.41

c. Lead Tetrachloride, $PbCl_4.3C_6H_5NH_2$.—Aniline gave a dark green, stable compound with lead tetrachloride in dilute solution. A more concentrated solution of the lead salt reacts very violently with aniline, probably giving rise to the same chlorinated products as tin tetrachloride, such as violaniline, mauvaniline, rosaniline, and triphenylendiamine blue—Girard and Pabst.[1] The dark green compound analyzed for three molecules of aniline.

0.2104 gram material gave:

0.1950 gram silver chloride = 0.0483 gram chlorine = 22.94 per cent. chlorine.

0.2042 gram material gave:

0.0963 gram lead sulphate = 0.0658 gram lead = 32.22 per cent. lead.

0.4012 gram material gave:

0.1929 gram platinum = 0.0277 gram nitrogen = 6.90 per cent. nitrogen.

	Calculated for $PbCl_4.3C_6H_5NH_2$.	Found.
Chlorine	22.61	22.94
Lead	32.96	32.22
Nitrogen	6.69	6.90

F. TOLUIDINE.

a. Zirconium Tetrachloride, $ZrCl_4.4C_6H_4CH_3NH_2$.—As aniline gave a derivative with zirconium tetrachloride, toluidine was also tried with like result. Analysis indicated that this compound contained four molecules of toluidine, showing it to be analogous to the aniline derivative.

0.3772 gram material gave:

0.3240 gram silver chloride = 0.0802 gram chlorine = 21.26 per cent. chlorine.

0.0694 gram zirconium dioxide = 0.0512 gram zirconium = 13.60 per cent. zirconium.

0.4296 gram material gave:

0.0456 gram ammonia = 0.0376 gram nitrogen = 8.74 per cent. nitrogen.

[1] *Bull. Soc. Chim.*, **34**, 33.

	Calculated for $ZrCl_4.4C_6H_4CH_3NH_2$.	Found.
Chlorine	21.50	21.26
Zirconium	13.72	13.60
Nitrogen	8.48	8.74

b. Thorium Tetrachloride, $ThCl_4.3C_6H_4CH_3NH_2$.—This was a greenish white precipitate and showed a departure from the other derivatives and from its analogous zirconium compound in that it only contained three molecules of the base.

0.5012 gram material gave:

0.4074 gram silver chloride = 0.1008 gram chlorine = 20.12 per cent. chlorine.

0.1940 gram thorium dioxide = 0.1705 gram thorium = 34.01 per cent. thorium.

0.7500 gram material gave:

0.0526 gram ammonia = 0.0433 gram nitrogen = 5.78 per cent. nitrogen.

	Calculated for $ThCl_4.3C_6H_4CH_3NH_2$.	Found.
Chlorine	20.41	20.12
Thorium	33.44	34.01
Nitrogen	6.04	5.78

c. Lead Tetrachloride.—With toluidine no additive product could be obtained, even by using quite dilute solutions of lead tetrachloride, as the amine was decomposed, giving a deep purple solution. Hence lead tetrachloride evidently has about the same action on toluidine as bleaching lime or tin tetrachloride.

G. PYRIDINE.

As pyridine and quinoline are strong bases, and as they may be considered tertiary amines, it was thought probable that these reagents would form derivatives with the tetrachlorides in a manner similar to aniline and toluidine. Experiment proved this surmise to be a correct one, as a compound was formed in both instances. It may be stated that Classen and Zahorski[1] have obtained compounds of lead tetrachloride with the hydrochlorides of pyridine and quinoline, and they are described as additive products. Goebbles[2] has also obtained compounds of lead tetrachloride with the salts of such complex organic bases as picoline, lutidine and collidine.

[1] *Ztschr. anorg. Chem.*, 4, 100.

[2] *Ber. d. chem. Ges.*, 28, 792.

The compounds of zirconium and thorium tetrachlorides with pyridine and quinoline are light gray to brown flocculent precipitates. Unlike the derivatives with the preceding amines, they appeared to be rather unstable in moist air, in consequence of which considerable difficulty was experienced in obtaining suitable portions for analysis, as the compounds had to be preserved under anhydrous ether.

a. Zirconium Tetrachloride, $ZrCl_4.2C_5H_5N$.—The best analysis that could be obtained for the pyridine derivative approximated to a formula containing two molecules of the base.

0.5420 gram material gave:

0.7805 gram silver chloride = 0.1932 gram chlorine = 35.64 per cent. chlorine.

0.1758 gram zirconium dioxide = 0.1299 gram zirconium = 23.97 per cent. zirconium.

0.6118 gram material gave:

0.0506 gram ammonia = 0.0417 gram nitrogen = 6.83 per cent. nitrogen.

	Calculated for $ZrCl_4.2C_5H_5N$.	Found.
Chlorine	36.35	35.64
Zirconium	23.19	23.97
Nitrogen	7.18	6.83

b. Thorium Tetrachloride, $ThCl_4.C_5H_5N$.—0.5002 gram material gave:

0.6270 gram silver chloride = 0.1552 gram chlorine = 31.02 per cent. chlorine.

0.2939 gram thorium dioxide = 0.2583 gram thorium = 51.64 per cent. thorium.

0.4107 gram material gave:

0.0126 gram ammonia = 0.0104 gram nitrogen = 2.53 per cent. nitrogen.

	Calculated for $ThCl_4.C_5H_5N$.	Found.
Chlorine	31.30	31.02
Thorium	51.28	51.64
Nitrogen	3.09	2.53

c. Lead Tetrachloride, $PbCl_4.2C_5H_5N$.—Pyridine gave a pale yellow precipitate with lead tetrachloride of much greater stability than the foregoing compounds.

0.2506 gram material gave:

0.2780 gram silver chloride = 0.0688 gram chlorine = 27.46 per cent. chlorine.

0.3125 gram material gave:

0.1842 gram lead sulphate = 0.1258 gram lead = 40.26 per cent. lead.

0.3062 gram material gave:

0.1112 gram platinum = 0.0161 gram nitrogen = 5.21 per cent. nitrogen.

	Calculated for $PbCl_4.2C_5H_5N$.	Found.
Chlorine	28.01	27.46
Lead	40.83	40.26
Nitrogen	5.52	5.21

H. QUINOLINE.

a. Zirconium Tetrachloride, $ZrCl_4.2C_9H_7N$. — 0.6140 gram material gave:

0.6977 gram silver chloride = 0.1727 gram chlorine = 28.12 per cent. chlorine.

0.1592 gram zirconium dioxide = 0.1177 gram zirconium = 19.17 per cent. zirconium.

0.7226 gram material gave:

0.0478 gram ammonia = 0.0394 gram nitrogen = 5.45 per cent. nitrogen.

	Calculated for $ZrCl_4.2C_9H_7N$.	Found.
Chlorine	28.94	28.12
Zirconium	18.47	19.17
Nitrogen	5.72	5.45

b. Thorium Tetrachloride, $ThCl_4.C_9H_7N$.—0.4110 gram material gave:

0.4634 gram silver chloride = 0.1147 gram chlorine = 27.91 per cent. chlorine.

0.2175 gram thorium dioxide = 0.1911 gram thorium = 46.50 per cent. thorium.

0.4212 gram material gave:

0.0129 gram ammonia = 0.0106 gram nitrogen = 2.52 per cent. nitrogen.

	Calculated for $ThCl_4.C_9H_7N$.	Found.
Chlorine	28.19	27.91
Thorium	46.18	46.50
Nitrogen	2.78	2.52

c. Lead Tetrachloride, $PbCl_4.2C_9H_7N$.—Quinoline reacted very energetically with lead tetrachloride, yielding a lemon-yellow precipitate which proved to be quite stable.

0.3012 gram material gave :

0.2806 gram silver chloride = 0.0695 gram chlorine = 23.06 per cent. chlorine.

0.2298 gram material gave :

0.1140 gram lead sulphate = 0.0779 gram lead = 33.90 per cent. lead.

0.2792 gram material gave :

0.0845 gram platinum = 0.0121 gram nitrogen = 4.34 per cent. nitrogen.

	Calculated for $PbCl_4.2C_9H_7N$.	Found.
Chlorine	23.39	23.06
Lead	34.10	33 90
Nitrogen	4.61	4.34

I. β-NAPHTHYLAMINE.

a. Zirconium Tetrachloride, $ZrCl_4.2C_{10}H_7NH_2$.—On adding a solution of naphthylamine in anhydrous ether to a solution of zirconium tetrachloride a grayish brown precipitate was produced, the analysis of which approximated to the formula given above.

0.5736 gram material gave :

0.6419 gram silver chloride = 0.1589 gram chlorine = 27.70 per cent. chlorine.

0.1397 gram zirconium dioxide = 0.1032 gram zirconium = 18.00 per cent. zirconium.

0.7012 gram material gave :

0.0426 gram ammonia = 0.0351 gram nitrogen = 5.01 per cent. nitrogen.

	Calculated for $ZrCl_4.2C_{10}H_7NH_2$.	Found.
Chlorine	27.38	27.70
Zirconium	17.47	18.00
Nitrogen	5.41	5.01

b. Thorium Tetrachloride, $ThCl_4.C_{10}H_7NH_2$.—This derivative was grayish white in color and comparatively stable in the air.

0.2582 gram material gave :

0.2844 gram silver chloride = 0.0704 gram chlorine = 27.27 per cent. chlorine.

0.1329 gram thorium dioxide = 0.1168 gram thorium = 45.25 per cent. thorium.

0.6045 gram material gave:

0.0166 gram ammonia = 0.0137 gram nitrogen = 2.27 per cent. nitrogen.

	Calculated for $ThCl_4.C_{10}H_7NH_2$.	Found.
Chlorine	27.43	27.27
Thorium	44.94	44.25
Nitrogen	2.70	2.27

c. Lead Tetrachloride, $PbCl_4.C_{10}H_7NH_2$.—Naphthylamine gave a dark green precipitate with lead tetrachloride in a dilute solution; in more concentrated solutions the naphthylamine was apparently decomposed.

0.2276 gram material gave:

0.2604 gram silver chloride = 0.0645 gram chlorine = 28.32 per cent. chlorine.

0.3006 gram material gave:

0.1914 gram lead sulphate = 0.1307 gram lead = 43.47 per cent. lead.

0.2416 gram material gave:

0.0544 gram platinum = 0.0079 gram nitrogen = 3.24 per cent. nitrogen.

	Calculated for $PbCl_4.C_{10}H_7NH_2$.	Found.
Chlorine	28.86	28.32
Lead	42.07	43.47
Nitrogen	2.84	3.24

J. ACID AMIDES.

The action of acetamide and benzamide was tried on the solutions of the tetrachlorides, but no compound resulted in any case, the acid amides evidently not being sufficiently basic to form derivatives like the amines.

Diphenylamine was also tried, but it gave no reaction with either the zirconium or thorium salt. The lead salt gave a deep blue solution and lead chloride separated out, showing that the lead tetrachloride in this case acted like bleaching lime on diphenylamine.

5. GENERAL REMARKS.

On comparing the derivatives of the three tetrachlorides here used, many similarities will at once be evident. In order to facilitate with such a comparison, it will not be superfluous to present a tabular résumé of the various derivatives herein prepared and described.

	With $ZrCl_4$ mols. amine.	With $ThCl_4$ mols. amine.	With $PbCl_4$ mols. amine.
Ammonia (from solution)	8	8	4, 2
Ammonia (without heat)	2	6	.
Ammonia (with heat)	4	6	.
Methylamine	4	4	4
Ethylamine	4	4	4
Propylamine	4	4	4
Aniline	4	4	3
Toluidine	4	3	decomp.
Pyridine	2	1	2
Quinoline	2	1	2
Naphthylamine	2	1	1
Diphenylamine	no reaction	no reaction	decomp.
Acid amides	no reaction	no reaction	no reaction

Nearly all these derivatives are stable in the air, the only noticeable exceptions being the pyridine, quinoline, and the lower ammonia compounds of zirconium and thorium. None of them show any tendency toward a crystalline structure, but come down as amorphous precipitates resembling hydroxides.

On heating these compounds in the air they readily split up into the amine hydrochloride and the dioxides; with lead, however, lead dichloride is left on ignition. They are also decomposed when treated with water, and the fixed alkalies precipitate the hydroxides of the three metals.

It will also be noticed that the majority of these derivatives seem to obey the law of Remsen in its application to molecular compounds; and the tendency is apparently toward an even number of molecules, though several of the thorium and lead derivatives deviate from this general law in having an odd number of additive molecules.

Two of the chlorine atoms in lead tetrachloride are very loosely combined, splitting off at the slightest disturbance to the chemical equilibrium of the compound; and yet it is of interest to note that the amines seem to fix these two atoms of

chlorine into a more stable form, doubtless due to some peculiar internal linking in the compound. That these two atoms of chlorine are exceedingly active is seen by the behavior of lead tetrachloride with toluidine, where no additive compound could be obtained, as the amine was decomposed even with dilute solutions, giving rise no doubt to complex chlorinated and condensed products. In fact, concentrated solutions of lead tetrachloride will decompose any of the aromatic amines, with the production of blue, purple, and green-colored solutions and resinous products. In this great activity of two of its atoms of chlorine, lead tetrachloride differs widely from the corresponding salts of zirconium and thorium, as these latter show no tendency to break down to lower chlorides.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 33.]

II. DERIVATIVES OF THE TETRABROMIDES OF ZIRCONIUM AND THORIUM.

BY J. MERRITT MATTHEWS.

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1. INTRODUCTION.

THIS investigation was taken up as an adjunct to the preceding research on the derivatives of the tetrachlorides.

Only derivatives with the four most typical amines—ammonia, ethylamine, aniline and pyridine—were prepared, as it was considered needless to extend the investigation further, when the aim was only to prove a general reaction between the amine bases and the tetrahalides of the fourth group.

The anhydrous tetrabromides of zirconium and thorium were prepared in a manner exactly similar to their tetrachlorides, dry bromine vapors in a current of carbon dioxide gas, being substituted for chlorine. Mellis[1] and Troost and Ouvrard.[2]

Owing to the slight solubility of the tetrabromides in any of the usual organic solvents, the reagents in all cases were added to the dry salts, any excess being removed by washing the product so formed with ether.

[1] *Zischr. Chem.* (2), 6, 296.

[2] *Ann. chim. phys.* (6), 17, 229.

Several attempts were made to prepare the tetrabromide of lead, proceeding in a manner analogous to that used in the preparation of the tetrachloride, but without success.

2. THE AMINE DERIVATIVES.

A. AMMONIA.

a. Zirconium Tetrabromide, $ZrBr_4.4NH_3$.—On passing dry ammonia gas over zirconium tetrabromide at a slightly elevated temperature, a white compound was formed.

0.5186 gram zirconium tetrabromide increased in weight to 0.6035 gram.

0.2246 gram of this compound, on analysis, gave:

0.3511 gram silver bromide = 0.1494 gram bromine = 66.50 per cent. bromine.

0.0584 gram zirconium dioxide = 0.0432 gram zirconium = 19.22 per cent. zirconium.

0.3024 gram material gave:

0.2426 gram platinum = 0.0422 gram ammonia = 13.96 per cent. ammonia.

	Calculated for $ZrBr_4.4NH_3$.	Found.
Bromine	66.80	66.50
Zirconium	18.96	19.22
Ammonia	14.23	13.96
	Gram.	Gram.
Increase in weight	0.0861	0.0849

b. Thorium Tetrabromide, $ThBr_4.3NH_3$.—This was prepared in the same manner as the zirconium compound, and was white in color.

0.4712 gram thorium tetrabromide, increased in weight to 0.5119 gram which, on analysis, gave:

0.6491 gram silver bromide = 0.2762 gram bromine = 53.96 per cent. bromine.

0.2273 gram thorium dioxide = 0.1997 gram thorium = 39.01 per cent. thorium.

	Calculated for $ThBr_4.3NH_3$.	Found.
Bromine	53.07	53.96
Thorium	38.47	39.01
	Gram.	Gram.
Increase in weight	0.0435	0.0407

B. ETHYLAMINE.

a. Zirconium Tetrabromide, $ZrBr_4.4C_2H_5NH_2$. — 0.2506 gram zirconium tetrabromide, treated with ethylamine, gave 0.3572 gram of a white compound which, on analysis, yielded:

0.4597 gram silver bromide = 0.1956 gram bromine = 54.75 per cent. bromine.

0.0769 gram zirconium dioxide = 0.0569 gram zirconium = 15.92 per cent. zirconium.

	Calculated for $ZrBr_4.4C_2H_5NH_2$.	Found.
Bromine	54.12	54.75
Zirconium	15.36	15.92
	Gram.	Gram.
Increase in weight	0.1098	0.1066

b. Thorium Tetrabromide, $ThBr_4.4C_2H_5NH_2$. — 0.3121 gram thorium tetrabromide, treated with ethylamine, gave 0.4098 gram of a white compound which, on analysis, yielded:

0.4246 gram silver bromide = 0.1807 gram bromine = 44.09 per cent. bromine.

0.1502 gram thorium dioxide = 0.1320 gram thorium = 32.21 per cent. thorium.

	Calculated for $ThBr_4.4C_2H_5NH_2$.	Found.
Bromine	43.71	44.09
Thorium	31.69	32.21
	Gram.	Gram.
Increase in weight	0.1018	0.0977

C. ANILINE.

a. Zirconium Tetrabromide, $ZrBr_4.4C_6H_5NH_2$.—0.2075 gram zirconium tetrabromide, treated with aniline, gave 0.4117 gram of a brownish colored compound which, on analysis, yielded:

0.3821 gram silver bromide = 0.1626 gram bromine = 40.47 per cent. bromine.

0.0631 gram zirconium dioxide = 0.0467 gram zirconium = 11.62 per cent. zirconium.

	Calculated for $ZrBr_4.4C_6H_5NH_2$.	Found.
Bromine	40.83	40.47
Zirconium	11.46	11.62
	Gram.	Gram.
Increase in weight	0.1911	0.1932

b. Thorium Tetrabromide, $ThBr_4.4C_6H_5NH_2$. — 0.2214 gram thorium tetrabromide, treated with aniline, gave 0.3675 gram of a brown-colored compound which, on analysis, yielded :

0.3032 gram silver bromide = 0.1290 gram bromine = 35.10 per cent. bromine.

0.1069 gram thorium dioxide = 0.0939 gram thorium = 25.56 per cent. thorium.

	Calculated for $ThBr_4.4C_6H_5NH_2$.	Found.
Bromine	34.63	35.10
Thorium	25.11	25.56
	Gram.	Gram.
Increase in weight	0.1492	0.1461

D. PYRIDINE.

a. Zirconium Tetrabromide, $ZrBr_4.2C_5H_5N$.—0.3551 gram zirconium tetrabromide, treated with pyridine, gave 0.3718 gram of a brown compound which, on analysis, yielded :

0.4876 gram silver bromide = 0.2075 gram bromine = 55.82 per cent. bromine.

0.0802 gram zirconium dioxide = 0.0604 gram zirconium = 16.24 per cent. zirconium.

	Calculated for $ZrBr_4.2C_5H_5N$.	Found.
Bromine	56.22	55.82
Zirconium	15.95	16.24
	Gram.	Gram.
Increase in weight	0.1357	0.1325

b. Thorium Tetrabromide, $ThBr_4.C_5H_5N$.—0.2817 gram thorium tetrabromide, treated with pyridine, gave 0.3343 gram of a brownish compound which, on analysis, yielded :

0.3960 gram silver bromide = 0.1685 gram bromine = 50.42 per cent. bromine.

0.1412 gram thorium dioxide = 0.1241 gram thorium = 37.11 per cent. thorium.

	Calculated for $ThBr_4.C_5H_5N$.	Found.
Bromine	50.71	50.42
Thorium	36.77	37.11
	Gram.	Gram.
Increase in weight	0.0403	0.0426

It will be noticed that these derivatives of the tetrabromides

correspond very closely to those of the tetrachlorides of these same elements in the number of molecules of the amine in combination with one molecule of the halogen salt.

It may be remarked that Classen and Zahorski[1] have obtained additive compounds of lead tetrabromide and lead tetraiodide with the hydrobromic and hydriodic acid salts of several of the organic amines, by decomposing the corresponding chlorine compounds with cooled solutions of potassium bromide or potassium iodide. Thus $PbCl_4.2(C_9H_7N.HCl)$ with potassium bromide gave $PbBr_4.2(C_9H_7N.HBr)$, and with potassium iodide, $PbI_4.2(C_9H_7N.HI)$.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 34.]

III. THE PREPARATION OF ZIRCONIUM NITRIDES.

BY J. MERRITT MATTHEWS.

Received September 2, 1898.

THE ammonia derivative of titanium tetrachloride, $TiCl_4.4NH_3$, when heated in a current of ammonia gas, yields a nitride of titanium; Rose,[2] Persoz.[3] This nitride has been given the formula Ti_3N_4, and has been thoroughly investigated. From this knowledge it was of interest to ascertain if a zirconium nitride could be prepared from its ammonia derivative. The attempt was made and a corresponding zirconium nitride was obtained.

A portion of the zirconium tetrachloride derivative with ammonia, $ZrCl_4.8NH_3$, obtained by passing dry ammonia gas into an ethereal solution of the zirconium salt,[4] was placed in a porcelain boat and gradually heated to redness in a current of nitrogen in a glass combustion tube. Abundant fumes of ammonium chloride were given off and condensed in the cooler part of the tube; the residue left in the boat was pearl-gray in color and in the form of a light powder. On heating this residue in a current of hydrogen, ammonia was evolved, which was conducted into a standardized solution of hydrochloric acid, and thus determined.

1 *Ztschr. anorg. Chem.*, 4, 100.
2 Pogg. *Ann.*, 16, 57.
3 *Ann. chim. phys.*, 44, 321.
4 This Journal, 20, 821.

When this compound was heated in the air it lost weight, and became pure white in color, passing over into the dioxide, ZrO_2, and the zirconium was estimated in this form.

ANALYSES.

I. 0.2416 gram material gave :

0.0836 gram ammonia = 0.0688 gram nitrogen = 28.47 per cent. nitrogen.

0.0654 gram material gave :

0.0629 gram zirconium dioxide = 0.0465 gram zirconium = 71.10 per cent. zirconium.

II. 0.2006 gram material gave :

0.0691 gram ammonia = 0.0569 gram nitrogen = 28.36 per cent. nitrogen.

0.2572 gram material gave :

0.2469 gram zirconium dioxide = 0.1827 gram zirconium = 71.05 per cent. zirconium.

These analyses show a close approximation to the formula Zr_3N_6.

	Calculated for Zr_3N_6.	Found. I.	II.
Zirconium	70.82	71.10	71.04
Nitrogen.....	29.18	28.47	28.36

The residue left after heating this nitride in a current of hydrogen, was lead-gray in color and amorphous; it was soluble in hydrofluoric acid, but proved to be insoluble in the other mineral acids. This appearance and behavior leave little doubt but that this residue consists of metallic zirconium, the action of hydrogen being to reduce the nitride to the metal with the formation of ammonia.

In the preparation of the pure nitride care must be exercised in excluding all air from the apparatus, otherwise a mixture of the oxide and nitride will be obtained. In the preparation of the sample used for the above analyses, all the air was first driven out by means of a vigorous current of carbon dioxide gas, after which a current of nitrogen was allowed to pass through the apparatus for two hours before the compound was heated.

Zr_2N_3.—This second nitride was prepared by a procedure differing somewhat from that used in the first. Zirconium tetrachloride was placed in a porcelain boat and gradually heated to

redness in a current of dry ammonia gas. By this method the ammonia derivative, $ZrCl_4.4NH_3$, was at first formed.[1] This by the action of heat was broken down into a nitride of zirconium together with the formation of ammonium chloride, which was given off in dense fumes and condensed in the cooler part of the tube, leaving the nitride in the boat in the form of a gray amorphous powder. It was somewhat darker in color than the preceding compound, but resembled it exactly in its behavior. The nitrogen was estimated by heating the compound in a current of hydrogen, and collecting the ammonia evolved in a standardized solution of hydrochloric acid. By heating another portion in the air it became pure white in color, increasing in weight, leaving the dioxide, ZrO_2, from the weight of which the zirconium was estimated.

ANALYSES.

I. 0.2537 gram material gave :

0.0478 gram ammonia = 0.0402 gram nitrogen = 19.23 per cent. nitrogen.

0.2462 gram material gave :

0.2707 gram zirconium dioxide = 0.2001 gram zirconium = 81.27 per cent. zirconium.

II. 0.2217 gram material gave :

0.0523 gram ammonia = 0.0431 gram nitrogen = 19.42 per cent. nitrogen.

0.2546 gram material gave :

0.2792 gram zirconium dioxide = 0.2064 gram zirconium = 81.05 per cent. zirconium.

	Calculated for Zr_3N_4.	Found. I.	Found. II.
Zirconium	81.18	81.27	81.05
Nitrogen.....	18.82	19.23	19.42

Mallet[2] obtained a nitride of zirconium by heating the metal in ammonia gas; it is described as a dark gray amorphous powder. A similar product, and one identical, in every way, with that obtained in this present research, was also prepared by Mallet, by heating anhydrous zirconium tetrachloride in ammonia gas. This procedure is exactly similar to that described

[1] This Journal, 20, 823.

[2] *Jsb. Chem.*, *18*5 145.

above; but Mallet made no investigation into the constitution of the compound which he prepared in this manner.

A nitride of thorium has been prepared by Chydenius[1] by a procedure identical with that used in the preparation of the first zirconium nitride above described. This nitride of thorium is spoken of as a white amorphous powder, and behaves in a manner very similar to the zirconium compound. Thus the analogy existing between these two elements is once more strikingly manifested.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 35.]

IV. ON THE SEPARATION OF IRON FROM ZIRCONIUM AND CERTAIN OTHER ALLIED METALS.

BY J. MERRITT MATTHEWS.

Received September 2, 1898.

THOUGH there have been several methods proposed in the past for the separation of iron from zirconium, still chemists have not considered that this problem has, as yet, been satisfactorily solved. All methods which have been recommended for the quantitative separation of these two metals have proved, in some particular, to be untrustworthy, for in all of them traces of iron appear to remain with the zirconium with great pertinacity.

As it may be of interest in connection with the present subject, a brief résumé will here be given of the principal methods which have hitherto been proposed for the separation of iron from zirconium.

Bailey,[2] by the use of a moderately concentrated solution of hydrogen peroxide precipitates Zr_2O_5, whereas neither iron, aluminum, nor titanium salts are precipitated by this reagent. No accurate results, however, have been worked out by this method.

Berlin[3] observes that if zirconium dioxide, contaminated with iron, is fused with sodium carbonate to a white heat, and the fusion treated with hydrochloric acid, the iron salt dissolves,

[1] *Jsb. Chem.*, *1863*, 194.
[2] *J. Chem. Soc.*, **49**, 481.
[3] *J. prakt. Chem.*, **58**, 147.

leaving the zirconium dioxide undissolved. Scheerer[1] claims that by this fusion a sodium zirconate is formed at first, which is subsequently decomposed on washing with water. Some of the zirconium, however, will go into the solution with the iron; and on the other hand, the zirconium dioxide will still be slightly contaminated with traces of ferric oxide.

Stromeyer[2] applies Chancel's method[3] for the separation of iron from aluminum to its separation from zirconium. By boiling with sodium thiosulphate, zirconium hydroxide is precipitated, while the iron remains in solution. Hermann,[4] however, says that this procedure results in the formation of a zirconium hyposulphite; and traces of iron still continue with the zirconium. For an approximate separation, however, this seems to be a good one.

Rivot[5] recommends the reduction of the iron to the metallic condition, by heating in a current of hydrogen. But it is very doubtful if all of the iron will be eliminated from the zirconium dioxide by this means.

Berthier[6] uses ammonium hydroxide and sulphide, which precipitates ferrous sulphide, FeS, and zirconium hydroxide, $Zr(OH)_4$; when this mixture is treated with sulphurous acid, the ferrous sulphide dissolves; the filtrate may contain some zirconium salt which, on heating, is precipitated from the iron as hydroxide. Hermann claims that this method does not give zirconium dioxide free from iron. Henneberg[7] obtains a zirconium dioxide pure, except in that portion which is precipitated on heating.

Hermann claims to have obtained very pure zirconium dioxide by treating a solution of the chloride with a corresponding amount of ammonium oxalate, and igniting the precipitate. But in this method the amount of zirconium must be known beforehand, in order to calculate the quantity of ammonium oxalate to be added, as any excess of the latter reagent will dissolve the precipitate.

[1] Pogg. *Ann.*, 59, 48.
[2] *Ann. Chem. Pharm.*, 113, 127.
[3] *J. prakt. Chem.*, 74, 471.
[4] *Ibid*, 97, 340.
[5] *Ann. chim. phys.*, 17, 244.
[6] *Ibid*, 50, 362.
[7] *J. prakt. Chem.*, 38, 508.

Dubois and Silveria observe that if impure zirconium hydroxide is boiled with oxalic acid, the iron oxalate formed is easily soluble, whereas the zirconium oxalate is insoluble. But Berlin[1] found that the zirconium oxalate is somewhat soluble in oxalic acid, which fact vitiates this method.

Classen[2] gives an electrolytic separation of iron from zirconium; but by his method the zirconium is only determined by difference.

Another method which has been recommended is to boil the impure zirconium salt with a solution of potassium sulphate, when a basic sulphate of zirconium will be precipitated. The precipitation, however, is never complete, as the filtrate always contains some of the zirconium.

It will be seen by this short review that the separation of iron from zirconium is by no means a positive certainty, as there seems to be a great many conflicting opinions entertained by the different authorities.

DETAILS OF THE METHOD FOR THE SEPARATION OF IRON FROM ZIRCONIUM.

On introducing a small quantity of water into an ethereal solution of zirconium tetrachloride, it was noticed that a white precipitate was formed, insoluble in excess of ether. This precipitate was no doubt an oxychloride of zirconium, and analyzed in accordance with the well-known hydrated chloride, $ZrOCl_2.8H_2O$.

I. 0.1682 gram material gave:

0.1492 gram silver chloride = 21.93 per cent. chlorine.

0.0645 gram zirconium dioxide = 28.34 per cent. zirconium.

II. 0.1276 gram material gave:

0.1181 gram silver chloride = 21.86 per cent. chlorine.

0.0488 gram zirconium dioxide = 28.26 per cent. zirconium.

	Calculated for $ZrOCl_2.8H_2O$.	Found. I.	II.
Chlorine	22.05	21.93	21.86
Zirconium	28.18	28.34	28.26

On testing this precipitate with a solution of potassium thiocyanate, not a trace of iron was indicated, although the zir-

[1] *J. prakt. Chem.*, 58, 145.

[2] *Ber. d. chem. Ges.*, 14, 2783.

conium tetrachloride used in the solution showed a decided contamination by iron under the same conditions.

With this sharp distinction in solubilities of the hydrated salts of zirconium and iron in ether as a basis, a simple and accurate separation of these two elements was immediately suggested.

Weighed quantities of the chlorides of zirconium and iron were mixed together. Previous analyses of these salts were made in order to determine their respective percentages of zirconium and iron. The mixed salts were dissolved in water and carefully evaporated to dryness on a water-bath; after cooling they were treated with absolute ether, and dry hydrochloric acid gas was passed through the liquid. Experience proved that this latter treatment was necessary to effect a rapid and complete solution of the iron salt by the ether, as the ferric chloride on evaporation to dryness evidently forms basic compounds of indefinite composition which are difficultly soluble in ether. The solution was rapidly filtered, and the residue washed with absolute ether several times to insure the removal of the last traces of the iron salt. The residue was then dissolved in water, and the zirconium determined by precipitation as hydroxide by means of ammonium hydroxide; drying the precipitate, igniting and weighing as zirconium dioxide, ZrO_2. The ether was evaporated or distilled from the filtrate, and the residue dissolved in water, with the addition of a few drops of hydrochloric acid if necessary; and the iron was determined by precipitation with ammonium hydroxide, drying the precipitate, igniting, and weighing as ferric oxide, Fe_2O_3.

On testing the aqueous solution of the residue containing the zirconium with potassium thiocyanate solution, not a trace of iron was discovered, showing that the separation had been a complete and successul one.

Several analyses were made, using varying relative amounts of the zirconium and iron salts.

I. 0.1824 gram ferric chloride with 0.1262 gram zirconium tetrachloride gave:

0.0540 gram ferric oxide = 29.50 per cent. ferric oxide.

0.0615 gram zirconium dioxide = 48.89 per cent. zirconium dioxide.

II. 0.1763 gram ferric chloride with 0.1890 gram zirconium tetrachloride gave :

0.0524 gram ferric oxide = 29.55 per cent. ferric oxide.

0.0920 gram zirconium dioxide = 48.83 per cent. zirconium dioxide.

III. 0.3064 gram ferric chloride with 0.1620 gram zirconium tetrachloride gave :

0.0910 gram ferric oxide = 29.60 per cent. ferric oxide.

0.0788 gram zirconium dioxide = 48.79 per cent. zirconium dioxide.

IV. 0.6564 gram ferric chloride with 0.2544 gram zirconium tetrachloride gave :

0.1931 gram ferric oxide = 29.36 per cent. ferric oxide.

0.1240 gram zirconium dioxide = 48.78 per cent. zirconium dioxide.

V. 0.1276 gram ferric chloride with 0.6924 gram zirconium tetrachloride gave :

0.0390 gram ferric oxide = 29.70 per cent. ferric oxide.

0.3385 gram zirconium dioxide = 49.04 per cent. zirconium dioxide.

On analyzing the ferric chloride used it gave 29.44 per cent. ferric oxide, while the zirconium chloride gave 48.97 per cent. zirconium dioxide. The latter salt also showed a contamination by iron equivalent to 0.16 per cent. ferric oxide, and in the percentages given in the above analyses, an allowance is made for this correction.

		Found.				
	Used.	I.	II.	III.	IV.	V.
Ferric oxide.....	29.44	29.50	29.55	29.60	29.36	29.70
Zirconium dioxide .	48.97	48.89	48.83	48.79	48.78	49.04

In making a practical use of this separation it is only necessary to obtain the two metals in solution in the form of chlorides and then the details as already given may be applied.

ON THE DELICACY OF THE SEPARATION OF IRON FROM ZIRCONIUM.

The fact that zirconium oxychloride is perfectly white in color should not be taken as a final indication that it is absolutely free from traces of iron ; and this should be borne in mind in the preparation of salts for atomic weight determinations. In order

to establish the accuracy of the method which has been described for the separation of iron from zirconium, a series of delicate experiments was carried out with the object of determining approximately the quantity, if any, of iron still remaining with the zirconium salt.

Zirconium tetrachloride, contaminated with iron, was treated with a little water in order to convert it into the oxychloride; it was then digested with ether, and a drop of hydrochloric acid added. The ether was filtered off and the perfectly white residue of zirconium oxychloride was washed several times with absolute ether to insure the removal of the last traces of the iron salt.

A solution of ferric chloride was made, one cc. of which contained 0.000001 gram ferric chloride. This was called solution No. 1.

Another solution of ferric chloride was made, one cc. of which contained 0.0000005 gram ferric chloride. This was called solution No. 2.

One cc. of solution No. 1 was placed in a test-tube, and to this were added one cc. of hydrochloric acid (sp. gr. 1.17), and one cc. of a solution of ten grams ammonium thiocyanate in 100 cc. of water, and the volume of the liquid was made up to ten cc. A slight pink color was noticed. One cc. of solution No. 2 was treated in the same manner, and a just perceptible pink tinge was observed.

One-tenth gram of zirconium tetrachloride was dissolved in five cc. of water, and treated as above; a dark red color immediately appeared.

One-tenth gram of the zirconium oxychloride as freed from iron, was dissolved in five cc. of water, and treated in a similar manner; a very slight pink tinge was perceptible. On comparing this with solutions No. 1 and No. 2, it was found that the intensity of coloration of the zirconium oxychloride solution was between that of the two iron solutions. From this it is to be concluded that the ratio between the amount of iron salt and that of the zirconium salt present in the zirconium oxychloride is approximately between the limits of 1 : 200,000 and 1 : 100,000.

The tetrachloride of zirconium, before its separation from iron, showed a percentage of the latter equivalent to about 0.16

per cent. ferric oxide. By the above comparison this percentage appears to be reduced to something approximately between the limits of 0.001 and 0.0005 per cent. The solution of hydrochloric acid used in these experiments was purified to such an extent that one cc., when treated with one cc. of the ammonium thiocyanate solution, on dilution to ten cc. gave no perceptible pink coloration.

The observations of those delicate tints were made immediately after mixing the solutions, and by comparison with an equal volume of distilled water. On standing for a time the colors were apparently discharged.

As thorium, cerium, and titanium belong to the same group as zirconium, and form corresponding hydrated oxychlorides insoluble in ether, the same method was applied in the separation of iron from these metals as with zirconium, and very good results were obtained. The method was carried out in every particular as already described, and was also extended to include lanthanum, neodymium, and praseodymium, as their hydrated chlorides were found to be insoluble in ether.

THORIUM FROM IRON.

The thorium salt used was the chloride, and its analysis gave 60.79 per cent. thorium dioxide, and was not appreciably contaminated with iron, so no correction was necessary in the percentages found.

I. 0.5608 gram thorium tetrachloride with 0.2246 gram ferric chloride gave :

0.3418 gram thorium dioxide = 60.95 per cent. thorium dioxide.

0.0657 gram ferric oxide = 29.25 per cent. ferric oxide.

II. 0.2681 gram thorium tetrachloride with 0.4625 gram ferric chloride gave :

0.1628 gram thorium dioxide = 60.72 per cent. thorium dioxide.

0.1364 gram ferric oxide = 29.53 per cent. ferric oxide.

III. 0.5072 gram thorium tetrachloride with 0.3217 gram ferric chloride gave :

0.3075 gram thorium dioxide = 60.63 per cent. thorium dioxide.

0.0952 gram ferric oxide = 29.59 per cent. ferric oxide.

IV. 1.0368 grams thorium tetrachloride with 0.7241 gram ferric chloride gave :

0.6318 gram thorium dioxide = 60.94 per cent. thorium dioxide.

0.2137 gram ferric oxide = 29.51 per cent. ferric oxide.

V. 0.1193 gram thorium tetrachloride with 0.6976 gram ferric chloride gave :

0.0720 gram thorium dioxide = 60.35 per cent. thorium dioxide.

0.2062 gram ferric oxide = 29.58 per cent. ferric oxide.

		Found.				
	Used.	I.	II.	III.	IV.	V.
Ferric oxide	29.44	29.25	29.53	29.59	29.51	29.58
Thorium dioxide...	60.79	60.95	60.72	60.63	60.94	60.35

CERIUM FROM IRON.

Cerium chloride was used, and its analysis gave 61.11 per cent. cerium dioxide.

I. 0.1098 gram cerium chloride with 0.3510 gram ferric chloride gave :

0.0669 gram cerium dioxide = 60.93 per cent. cerium dioxide.

0.1044 gram ferric oxide = 29.74 per cent. ferric oxide.

II. 0.1930 gram cerium chloride with 0.2574 gram ferric chloride gave :

0.1178 gram cerium dioxide = 61.04 per cent. cerium dioxide.

0.0758 gram ferric oxide = 29.45 per cent. ferric oxide.

III. 0.2240 gram cerium chloride with 0.2642 gram ferric chloride gave :

0.1367 gram cerium dioxide = 61.03 per cent. cerium dioxide.

0.0784 gram ferric oxide = 29.67 per cent. ferric oxide.

IV. 0.7532 gram cerium chloride with 0.1024 gram ferric chloride gave :

0.4598 gram cerium dioxide = 61.05 per cent. cerium dioxide.

0.0301 gram ferric oxide = 29.39 per cent. ferric oxide.

V. 0.1262 gram cerium chloride with 0.8436 gram ferric chloride gave :

0.0774 gram cerium dioxide = 61.33 per cent. cerium dioxide.
0.2489 gram ferric oxide = 29.52 per cent. ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29.44	29.74	29.45	29.67	29.39	29.52
Cerium dioxide	61.11	60.93	61.04	61.03	61.05	61.33

TITANIUM FROM IRON.

Titanium chloride was the salt used, and on analysis this gave 57.17 per cent. titanium dioxide.

I. 0.1060 gram titanium chloride with 0.2224 gram ferric chloride gave:

0.0604 gram titanium dioxide = 56.98 per cent. titanium dioxide.

0.0660 gram ferric oxide = 29.68 per cent. ferric oxide.

II. 0.2588 gram titanium chloride with 0.2508 gram ferric chloride gave:

0.1474 gram titanium dioxide = 56.95 per cent. titanium dioxide.

0.0736 gram ferric oxide = 29.35 per cent. ferric oxide.

III. 0.6532 gram titanium chloride with 0.1086 gram ferric chloride gave:

0.3728 gram titanium dioxide = 57.08 per cent. titanium dioxide.

0.0318 gram ferric oxide = 29.28 per cent. ferric oxide.

IV. 0.3549 gram titanium chloride with 0.7643 gram ferric chloride gave:

0.2033 gram titanium dioxide = 57.28 per cent. titanium dioxide.

0.2253 gram ferric oxide = 29.48 per cent. ferric oxide.

V. 0.1083 gram titanium chloride with 0.9212 gram ferric chloride gave:

0.0617 gram titanium dioxide = 56.97 per cent. titanium dioxide.

0.2720 gram ferric oxide = 29.53 per cent. ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29.44	29.68	29.35	29.28	29.48	29.53
Titanium dioxide ..	57.17	56.98	56.95	57.08	57.28	56.97

LANTHANUM FROM IRON.

The lanthanum chloride used in the analyses gave 50.20 per cent. lanthanum oxide, La_2O_3.

I. 0.2968 gram lanthanum chloride with 0.1465 gram ferric chloride gave:

0.1485 gram lanthanum oxide, La_2O_3, = 50.03 per cent. lanthanum oxide.

0.0435 gram ferric oxide = 29.69 per cent. ferric oxide.

II. 0.4541 gram lanthanum chloride with 0.7105 gram ferric chloride gave:

0.2274 gram lanthanum oxide, La_2O_3, = 50.08 per cent. lanthanum oxide.

0.2098 gram ferric oxide = 29.53 per cent. ferric oxide.

III. 0.1079 gram lanthanum chloride with 0.6514 gram ferric chloride gave:

0.0539 gram lanthanum oxide, La_2O_3, = 49.95 per cent. lanthanum oxide.

0.1926 gram ferric oxide = 29.57 per cent. ferric oxide.

IV. 0.7525 gram lanthanum chloride with 0.1024 gram ferric chloride gave:

0.3769 gram lanthanum oxide, La_2O_3, = 50.09 per cent. lanthanum oxide.

0.0304 gram ferric oxide = 29.68 per cent. ferric oxide.

V. 0.5048 gram lanthanum chloride with 0.5025 gram ferric chloride gave:

0.2539 gram lanthanum oxide, La_2O_3, = 50.30 per cent. lanthanum oxide.

0.1485 gram ferric oxide = 29.55 per cent. ferric oxide.

		Found.				
	Used.	I.	II.	III.	IV.	V.
Ferric oxide	29.44	29.69	29.54	29.57	29.68	29.55
Lanthanum oxide, La_2O_3	50.20	50.03	50.08	49.95	50.09	50.30

PRASEODYMIUM FROM IRON.

The salt used was praseodymium nitrate, and its analysis gave 43.33 per cent. praseodymium oxide, Pr_2O_3.

I. 0.5308 gram praseodymium nitrate with 0.4245 gram ferric chloride gave:

0.2293 gram praseodymium oxide, Pr_2O_3, = 43.20 per cent. praseodymium oxide.

0.1261 gram ferric oxide = 29.70 per cent. ferric oxide.

II. 0.5090 gram praseodymium nitrate with 0.3596 gram ferric chloride gave:

0.2198 gram praseodymium oxide, Pr_2O_3, = 43.18 per cent. praseodymium oxide.

0.1064 gram ferric oxide = 29.59 per cent. ferric oxide.

III. 0.1085 gram praseodymium nitrate with 0.7240 gram ferric chloride gave:

0.0465 gram praseodymium oxide, Pr_2O_3, = 42.86 per cent. praseodymium oxide.

0.2139 gram ferric oxide = 29.54 per cent. ferric oxide.

IV. 0.6849 gram praseodymium nitrate with 0.1096 gram ferric chloride gave:

0.2960 gram praseodymium oxide, Pr_2O_3, = 43.33 per cent. praseodymium oxide.

0.0323 gram ferric oxide = 29.43 per cent. ferric oxide:

V. 0.2532 gram praseodymium nitrate with 0.2485 gram ferric chloride gave:

0.1092 gram praseodymium oxide, Pr_2O_3, = 43.13 per cent. praseodymium oxide.

0.0735 gram ferric oxide = 29.58 per cent. ferric oxide.

		Found.				
	Used.	I.	II.	III.	IV.	V.
Ferric oxide	29.44	29.70	29.59	29.54	29.43	29.58
Praseodymium oxide, Pr_2O_3 ...	43.33	43.20	43.18	42.86	43.22	43.13

NEODYMIUM FROM IRON.

Neodymium nitrate was used, and its analysis gave 42.20 per cent. neodymium oxide, Ne_2O_3.

I. 0.1763 gram neodymium nitrate with 0.4286 gram ferric chloride gave:

0.0740 gram neodymium oxide, Ne_2O_3, = 41.97 per cent. neodymium oxide.

0.1261 gram ferric oxide = 29.42 per cent. ferric oxide.

II. 0.6389 gram neodymium nitrate with 0.1842 gram ferric chloride gave:

0.2688 gram neodymium oxide, Ne_2O_3, = 42.07 per cent. neodymium oxide.

0.0540 gram ferric oxide = 29.32 per cent ferric oxide.

III. 0.7246 gram neodymium nitrate with 0.7562 gram ferric chloride gave :

0.3051 gram neodymium oxide, Ne_2O_3, = 42.11 per cent. neodymium oxide.

0.2229 gram ferric oxide = 29.48 per cent. ferric oxide.

IV. 0.1545 gram neodymium nitrate with 0.2046 gram ferric chloride gave :

0.0645 gram neodymium oxide, Ne_2O_3, = 41.75 per cent. neodymium oxide.

0.0610 gram ferric oxide = 29.81 per cent. ferric oxide.

V. 0.2081 gram neodymium nitrate with 0.7680 gram ferric chloride gave :

0.0869 gram neodymium oxide, Ne_2O_3, = 41.76 per cent. neodymium oxide.

0.2271 gram ferric oxide = 29.57 per cent. ferric oxide.

		Found.				
	Used.	I.	II.	III.	IV.	V.
Ferric oxide	29.44	29.42	29.32	29.48	29.81	29.57
Neodymium oxide, Ne_2O_3	42.20	41.97	42.07	42.11	41.75	41.76

The praseodymium and neodymium salts existing originally as nitrates, were evaporated to dryness with hydrochloric acid in order to convert them into the chloride form.

GENERAL REMARKS.

Gooch and Havens, in the *American Journal of Science* for December, 1896, describe a method for the separation of aluminum from iron by treatment with anhydrous ether saturated with hydrochloric acid gas. The hydrated chloride of aluminum remains insoluble, whereas the ferric salt is completely dissolved. This method is practically the same as the one herein described for the separation of iron from zirconium and the other rare earths ; but the results of this present research were mostly obtained in October and November, 1896, before the writer was aware of the contemporaneous work of Gooch and

Havens. These latter writers also describe a separation of aluminum from glucinum by the same method.[1]

The use of absolute ether may militate somewhat against the practical application of this method to general analytical purposes; since in the case of most of the metals experimented upon, very good separations are already known which do not require the use of a reagent both difficult and unpleasant to manipulate. This method, however, is especially recommended for the separation of iron from zirconium, the separations of the other metals being only tried as a matter of interest through the analogy existing between those metals and zirconium. A point, however, which may prove of practical importance, and which it is most desirable to emphasize here, is that by carefully following out the procedure herein described, zirconium oxychloride and dioxide may be easily and quickly prepared perfectly free from iron. This fact may be of considerable importance and utility in the preparation of zirconium compounds for use in atomic weight determinations, where a high degree of purity is absolutely necessary in order to obtain authentic results.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE LABORATORY OF THE NORTH DAKOTA AGRICULTURAL COLLEGE, NO. 1.]

THE PROTEIDS OF CREAM.

BY E. F. LADD.

Received September 28, 1898.

IN some preliminary work in the chemistry of ripening cream for butter-making, several methods for the separation of proteids were tried, some of which were not suited to this work, and the results may be of interest, if not of value, to other workers in the same line. In the work here presented it was not our purpose to determine each of the individual proteids that cream might contain, but rather to learn something of the changes that take place in the proteids of cream during the process of ripening.

For our purpose the proteids of milk were divided into four groups, casein, albumen, albumoses, and peptones; that is, the

[1] *Am. J. Sci.*, August, *1897*.

methods employed brought down whatever of proteids were present in one of these four groups, and no attempt was made to determine the globulins, etc. The methods employed for the separation of these groups were as follows:

Casein.—About ten grams of cream were diluted with eighty cc. of water and three cc. of a saturated alum solution added, the whole well stirred and then allowed to stand for ten minutes, then filtered and washed with hot water and the nitrogen determined in the residue by means of the Kjeldahl method.

Acetic acid was first employed as the precipitant for casein. This worked well on fresh cream, but on the ripened and sour cream no concordant results could be depended on and the filtration was very difficult.

Albumen.—The filtrate from the casein was then heated to boiling, allowed to stand for a few minutes, then filtered and washed with hot water and the nitrogen determined as in casein. Other methods were tried, such as tannin solution, sodium chloride, and tannic acid, but these methods were not found suited for the separation of albumen in the presence of proteoses, although in other lines of work they gave fairly good results.

Albumoses.—The filtrate from the last was evaporated to a small bulk, say fifty to sixty cc., and the solution then saturated with zinc sulphate. After standing for ten to twelve hours it was filtered, the precipitate well washed, and the nitrogen determined as before.

For separating albumoses, ammonium sulphate was first employed, but with a product like milk or cream, we found it impossible to make quantitative separations by means of this reagent, as it was impossible to get rid of all traces of salt without losing a considerable per cent. of the albumoses themselves. The method proved valuable, however, for separating quantities for dialyses to be purified and used in proximate analyses, or for further separating into the several albumoses.

Peptones.—The filtrate from the above was then evaporated to a small bulk, removing thereby a portion of the zinc salt and absolute alcohol to eighty per cent. of the volume added. After standing twelve hours, filtering and washing with alcohol, the nitrogen was determined.

Further experiments are necessary to determine whether the filtrate may be safely concentrated for the peptones without any loss of proteids. The loss in this case could have been but little, if any, but some work with urines indicated that a loss might result. This point will be further tested. The total nitrogen having been previously determined in the cream, we have a check on our work, and in our studies the sum of the nitrogen in the several precipitates have agreed very closely with the total nitrogen in the cream. Having found methods that would give fairly close results on known products, we next proceeded to determine the changes in the proteids of cream during the process of ripening.

A large number of determinations were made, always with about the same general results, therefore two cases will suffice for this study. No. 1 is for a fresh cream but four hours from time of drawing the milk from the cow's udder. The cream was separated by means of the centrifugal separator.

No. 2 is for a sample of cream well ripened, quite sour and ready for churning. The per cent. of nitrogen is given in each case.

	No. 1. Fresh. Per cent.	No. 2. Ripened. Per cent.
Nitrogen in casein	0.237	0.249
" " albumen	0.035	0.027
" " albumoses	0.031	0.033
" " peptones	0.023	0.032
Total nitrogen	0.326	0.341
Total nitrogen in cream	0.335	0.344
Loss	0.009	0.003

From the above it will be seen that the loss in working by these methods was not great, and further that there is not a very marked change in the proteids of cream during the process of ripening. Further studies may show that the product precipitated as casein in case of the ripened cream differs somewhat from that precipitated from the fresh cream. Such seemed to be the case, but the purified product from fresh and ripened cream has not been fully studied. Further results, together with other studies in milk and cream, will be given later in the form of a station publication.

AGRICULTURAL COLLEGE, N. D.,
September 3, 1898.

[CONTRIBUTION FROM THE LABORATORY OF THE NORTH DAKOTA AGRICULTURAL COLLEGE, NO. 2.]

HUMATES AND SOIL FERTILITY.

BY E. F. LADD.

Received September 28, 1898.

PREVIOUS to the time of Liebig it was quite generally supposed that plants derive their food principally from the humus of the soil, but after Liebig showed that the greater part of plant food was derived from the atmosphere, humus received less attention at the hands of chemists and other investigators, possibly less than it deserved. Agriculturists, however, have assigned a high place to humus in the soil, recognizing that it played an important part in modifying the physical conditions of the soil, in relation of soils to the water content as well as to the soil temperature. Chemists gave so little attention to this that in soil analyses humus has not been generally estimated, and almost no determinations have been made of the relation of humus to the mineral matter, or in other words the amounts and kinds of mineral constituents contained in the humates, or whether any relation existed between the amount of phosphates, potash, lime, and nitrogen contained in the soil humates and the productivity of the soil. We do not even know what humus is except that it is a very complex product. It would seem that a product so highly prized by the farmer as a constituent of his soil, should be worthy of most careful study. Snyder has given considerable attention to the subject of humus in the soil and humus products. In this article an attempt will be made to trace a relationship between the humates and soil fertility, and to show the necessity for a fuller consideration of the humates by the soil analyst. Although my own observations and experiments have extended over a period of eight years and many determinations have been made at different dates during this time, as other duties have permitted, work in this field has only just reached the point of showing where work must begin without having accomplished anything definite more than a strong conviction of the necessity for a most careful and painstaking investigation

of the humus question, especially in any investigation of the soils of North Dakota.

If by placing on record at this time the data secured during the past few months other workers are interested in soils and induced to take up the work, I shall have accomplished my object. The study of data presented by different workers will enable us to determine what are general principles and what results peculiar to local conditions. The soils of North Dakota contain such quantities of humus and organic matter that many problems can only be studied on soils from other places in order to determine some of the most important facts in connection with the humus problem.

In the following table are given results for twenty-four samples of soils, showing the per cent. of humates and humus, also the per cent. of total phosphates, lime, potash, and nitrogen contained in the soil, together with the amounts extracted as humates.

			Nitrogen.		Phosphoric acid, P_2O_5.		Lime, CaO.		Potash, K_2O.	
Soil.	Humates.	Humus.	Total.	In humus.	Total.	In humus.	Total.	In humus.	Total.	In humus.
411	6.85	4.03	0.340	0.163	0.29	0.086	0.58	0.336	0.32	0 110
413	9.20	4.45	0.390	0.193	0.37	0.168	0.37	0.263	0.51	0.201
414	5.92	2.54	0.190	0.152	0.16	0.097	0.40	0.210	0.21	0.083
415	8.02	3.94	0.200	0.140	0.30	lost	0.80	lost	0.30	lost
416	8.86	3.66	0.300	0.146	0.26	0.184	2.48	0.680	0.18	0.089
417	5.37	3.20	0.310	0.152	0.29	0.116	0.94	0.453	0.19	0.136
419	7.42	4.06	0.345	0.105	0.27	0.161	2.70	0.159	0.42	0.139
420	3.84	1.56	0.187	0.041	0.37	0.179	2.10	0.892	0.22	0.075
421	4.27	2.53	0.234	0.094	0.31	0.192	2.00	1.030	0.18	0.089
422	5.79	4.10	0.218	0.111	0.27	0.199	1.25	1.010	0.45	....
423	15.26	7.73	0.390	0.176	0.33	0.132	0.83	0.370	0.44	0.200
424	14.57	7.25	0.250	0.152	0.38	0.184	0.80	0.420	0.60	0.204
425	14.81	7.90	0.300	0.176	0.40	0.143	0.86	0.343	0.73	0.200
426	14.20	7.86	0.396	0.175	0.38	0.117	1.01	0.476	0.54	0.200
427	14.65	7.01	0.300	0.133	0.39	0.139	0.85	0.429	0.63	0.233
428	14.81	6.92	0.456	0.183	0.39	0.161	1.05	0.389	0.50	0.180
270*a*	7.40	4.78	0.220	0.157	0.14	0.110	trace	0	0.44	....
270*b*	7.32	4.18	0.310	0.256	0.24	0.137	0.64	0.423	0.25	....
86*a*	7.57	4.21	0.250	0.169	0.18	0.120	0.47	0.209	0.55	....
86*b*	5.85	3.33	0.180	0.123	0.20	0.103	0.34	0.170	0.35	....
277*a*	9.99	6.43	0.360	0.284	0.16	0.092	0.33	0.186	0.23	....
277*b*	11.10	4.89	0.450	0.362	trace	trace	1.12	0.609	0.42	....
81*a*	7.65	4.20	0 250	0.170	0.18	0.117	0.91	0.513	0.59	....
81*b*	8.94	3.80	0.180	0.115	0.20	0.225 ?	0.79	0.453	0.58	....

The soils examined were from various parts of the state, mostly outside of the valley, excepting 423 to 428 inclusive, which were

from the agricultural college farm, and represent principally soils from the plots where crop rotation experiments are being conducted. It will be seen that there is quite a range of variation for the different constituents in the twenty-four samples. This variation may best be shown in tabular form.

			Nitrogen.		Phosphoric acid, P_2O_5.		Lime, CaO.		Potash, K_2O.	
In twenty-four samples.	Humus.	Humates.	Total.	In humus.	Total.	In humus.	Total.	In humus.	Total.	In humus.
Minimum.	3.84	1.56	0.180	0.041	trace	0.086	trace	0	0.18	0.075
Maximum	15.26	7.90	0.456	0.362	0.40	0.199	2.70	1.03	0.73	0.233
Average ..	9.15	4.77	0.292	0.163	0.269	0.138	0.944	0.436	0.409	0.153

Phosphoric acid for 81*b* has been excluded, as evidently there is an error in one of the sets of determinations, although good duplicates are shown for each set. From this table it is evident that there is quite a range of mineral matter in the humates, and that a varying proportion of these constituents exist in the humates as compared with the total in the soil. The next table shows the per cent. of these several constituents that existed in the humates as compared with the total in the soil.

PER CENT. OF THE TOTAL IN THE HUMATES.

Number.	Nitrogen.	Phosphate, P_2O_5.	Lime, CaO.	Potash, K_2O.	Humus.
411	47.9	29.7	57.9	34.3	58.9
413	49.5	45.4	71.1	39.4	48.3
414	80.0	60.6	52.5	39.5	42.9
415	70.0	...	...	...	49.1
416	48.6	70.7	27.4	49.4	41.3
417	49.0	40.0	48.0	71.6	59.5
419	30.4	59.6	5.88	33.1	54.7
420	21.9	45.9	42.4	34.1	40.6
421	40.1	61.9	51.5	49.4	59.2
422	50.9	73.6	80.8	...	70.8
423	45.1	40.0	44.6	45.4	51.3
424	60.8	48.4	52.5	34.0	49.7
425	58.6	35.7	39.8	27.4	53.4
426	44.4	30.8	47.1	37.0	55.3
427	44.3	35.6	40.4	36.9	47.8
428	40.1	41.3	37.0	36.0	46.7
270*a*	71.3	78.6	0	...	64.6
270*b*	82.5	56.9	66.1	...	57.1
86*a*	67.6	66.6	44.5	...	55.6
86*b*	68.3	51.5	50.0	...	56.9
277*a*	78.9	57.5	56.3	...	64.6
277*b*	80.4	trace	54.4	...	44.0
81*a*	68.0	65.0	56.3	...	56.2
81*b*	63.9	112(?)	57.3	...	42.5
Average	55.8	51.3	46.2	37.4	52.1

If we represent the figures given in a form to show the amounts per acre, assuming that one acre of soil to the depth of one foot weighs 2,225,000 pounds, then for nitrogen we have:

NITROGEN PER ACRE.

	Total in soil. Pounds.	In humus. Pounds.
Highest	10,146	8,054
Lowest	4,005	912
Average	6,497	3,627

In the same manner excluding the soil when there was almost an absence of phosphates, we have for phosphoric acid:

PHOSPHORIC ACID (P_2O_5) PER ACRE.

	Total in soil. Pounds.	In humus. Pounds.
Highest	8,900	4,428
Lowest	3,115	1,913
Average	5,985	3,061

Here we find marked differences, and when we come to study the character of the humus itself, we find other conditions not yet understood, and which we do not care to consider at the present time. The unqualified term *humus* conveys but little more meaning than the term soil without any specifications as to kind and properties.

INFLUENCE OF CONTINUOUS CROPPING.

A field that has been continuously cropped for seventeen years in succession, occasionally to oats, but principally to wheat, began to show a marked decrease in yield. The soil is quite light, containing considerable sand, in fact it would be classed as a sandy loam. A field adjoining had never been broken, and originally the two fields were alike in general appearance, as I am informed by the proprietor. The ordinary soil analyses gave results as follows:

	Old soil. Cropped seventeen years. No. 420.	New soil. Unbroken prairie. No. 421.
Moisture	2.76	2.74
Sand, silica, etc	72.58	75.50
Soluble silica, SiO_2	11.73	9.65
Volatile matter	5.26	6.30
Potash, K_2O	0.22	0.18
Soda, Na_2O	0.42	0.66
Lime, CaO	2.10	2.00
Magnesia, MgO	0.08	0.07
Manganese, Mn_2O_3	trace	trace
Iron, Fe_2O_3	0.22	0.20
Alumina, Al_2O_3	3.41	2.19
Phosphoric acid, P_2O_5	0.37	0.31
Sulphuric acid, SO_3	0.79	0.72
Nitrogen	0.187	0.234

Until the last three or four crops the field had been a good producer, and an examination of the results above indicates very little as to the probable reason for the loss of productive power. The nitrogen is lower than the average for the state, but no lower than for the same group of soils in the state, and not nearly so low as in many fertile soils from other states. Of phosphates there is a good supply. Taking all things into consideration, I should find it difficult, if not quite impossible from the above analyses, to determine which field had been longest cropped.

An examination for the soil humus was then made with results as follows:

PER CENT.

	Old soil. No. 420.	New soil. No. 421.
Humates	3.04	4.27
Humus	1.56	2.53
Phosphoric acid, P_2O_5	0.179	0.192
In the Humates:		
Lime, CaO	0.892	1.030
Potash, K_2O	0.075	0.089
Nitrogen	0.041	0.094

The amount of humus originally in the soil was exceptionally low for a North Dakota soil, but by continuous cropping it has been reduced thirty-nine per cent., while the nitrogen of the humus has been reduced fifty-six per cent., leaving so small an amount of humus and of nitrogen in the humates that it is ques-

tionable whether the soil would supply proper food for the growing crop. We find similar conditions, but to a less marked degree in the other mineral constituents of the soil. This investigation of the humus, even with our lack of knowledge of the true nature of humus and humates, throws great light upon the character of the soil and the possible cause for a declining crop.

RELATION OF MINERAL MATTER TO HUMUS.

Does the mineral matter of the humates change with the decrease and increase of humus in the soil? The soil that we have just examined answers in part this question, but examinations made with the soils from the college farm showed in 1891 that the average humus content for the fields that had produced wheat for fifteen years was 126,000 pounds per acre, taken to a depth of one foot, while for surrounding unbroken prairie the average gave 218,000 pounds per acre, a loss by continuous cropping, burning of stubbles, etc., of 92,000 pounds, or of 42.2 per cent.

In another case where both the humus and phosphoric acid in the humates had been determined, we find:

PER CENT.

	Humus.	P_2O_5 in humates.
1891	5.35	0.079
1894	6.82	0.091
1898	7.86	0.117

For fifteen years previous to 1891 it is said the field had been cropped continuously to wheat. Beginning with 1892 a system of crop rotation has been followed, and the productivity of the field has continued to increase.

An acre of this soil then to the depth of one foot contained of humus and of phosphoric acid, P_2O_5, in the humates:

	Humus. Pounds.	P_2O_5 in humates. Pounds.
1891	119,037	1,758
1894	151,745	2,025
1898	174,885	2,603

The gain in humus from 1891 to 1898 has been 46.9 per cent., while the gain of phosphoric acid in the form of humates

has been forty-eight per cent. It will be observed that the gain in phosphoric acid in the humates has been expressed as per cent. almost the same as the gains for the humus in the same period. It has also been shown by Snyder[1] that when prepared humus is added to soils it combined with the mineral matter of the soil, forming humates.

If we calculate the nitrogen to show per cent. in humus, and the other mineral constituents to per cent. in humates, we shall have other relations brought out in a way not shown by the previous tables.

TABLE SHOWING PER CENTS.

		In humates.		
Number.	Nitrogen in humus.	Phosphoric acid, P_2O_5.	Lime, CaO.	Potash, K_2O.
411	4.43	1.26	4.03	1.62
413	4.33	1.82	2.85	4.48
414	5.93	1.63	3.74	1.48
415	3.55	...	...	...
416	3.98	2.09	7.82	1.01
417	4.87	2.14	8.32	2.51
419	1.41	2.17	2.14	1.90
420	1.07	4.66	25.57	1.98
421	2.20	4.49	24.12	2.08
422	1.91	3.43	17.44	...
423	2.26	0.87	2.42	1.36
424	2.13	1.26	2.94	1.37
425	2.22	0.96	2.31	1.35
426	2.23	0.83	3.35	1.40
427	1.90	0.92	3.01	1.60
428	2.65	1.08	2.65	1.20
270*a*	3.30	1.48	0	....
270*b*	6.01	1.87	5.79	....
86*a*	4.02	1.56	2.74	....
86*b*	3.68	1.80	2.90	....
277*a*	4.42	0.94	1.81	....
277*b*	7.40	trace	5.39	....
81*a*	4.00	1.54	5.71	....
81*b*	3.03	2.05	5.07	....

Other experiments are now in progress to answer some of the many questions that have been suggested by the foregoing.

AGRICULTURAL COLLEGE, N. D., September 20, 1898.

[1] This Journal, 19, 738.

THE LE SUEUR PROCESS FOR THE ELECTROLYTIC PRODUCTION OF SODIUM HYDROXIDE AND CHLORINE.[1]

By Charles Lathrop Parsons.

Received September 17, 1898.

HISTORY.

ERNEST A. LE SUEUR enjoys the distinction of having invented the first electrolytic process for the commercial decomposition of sodium chloride, which became a regular contributor to the markets of the world. Since February, 1893, caustic soda and bleaching powder have been manufactured at Rumford Falls, Maine, on a commercial scale. Le Sueur is now general manager of the plant, and deserves the highest credit for his efforts in this important branch of chemical science and industry.

He first began his experiments in the winter of 1887–88, and after associating with him Charles N. Waite, who afforded him valuable assistance and some facilities at his chemical works at Newton, Mass., they together ran an experimental cell from October, 1890, to May, 1891, in a paper mill at Bellows Falls, Vermont. In the meantime, Le Sueur had applied for his patents, and having obtained a cell giving an efficiency of rising seventy per cent., he went to England in May, 1891, for the purpose of presenting his process at the seat of the alkali industry. There he met with much encouragement from scientific men, but with discouragement so far as the adoption of his method on a commercial scale was concerned. The article of Cross and Bevan[2] gives a good description of the method at the time, but as theirs is the only authoritative article ever published regarding the process, it is not at all strange that Lunge[3] has some doubts of a method which must renew its diaphragms every forty-eight hours, and which converts its caustic solution into bicarbonate. As a matter of fact, carbonate of soda, as sodium carbonate or acid carbonate, has never been a product and the diaphragms are renewed so seldom that their cost is a mere incident of the process.

[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

[2] *J. Soc. Chem. Ind.*, December, *1892*.

[3] Alkali Industry, Vol. III.

In 1892, an association was formed, which in August of that year began the erection of a plant at Rumford Falls, and in February, 1893, began the manufacture of caustic soda and bleaching powder, using, to generate the required electricity, one 200 kilowatt dynamo of the Thompson–Houston pattern. The success of the venture was such that three more dynamos of the same capacity were installed in the fall of 1894, and the Electro-Chemical Company was organized. As a member of that company since its inception, I am fortunate in having the cooperation of Mr. Le Sueur and in being authorized to present to you a description of the process as it is running to-day, with such comments on past experience as I may deem of interest to you.

THE PROCESS.

The first practical working cell devised and used is well illustrated in the accompanying figure (Fig. 1), and is much the

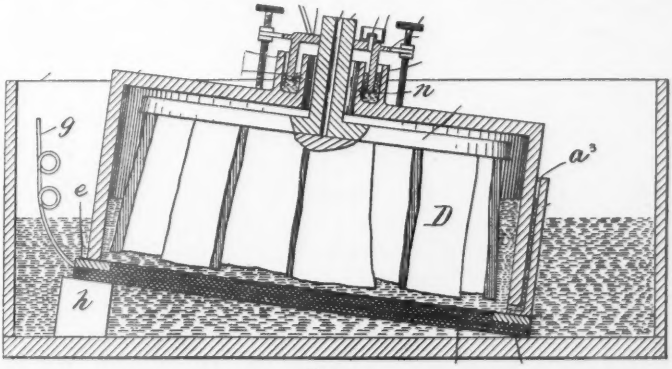

FIG. 1.

same as that described by Cross and Bevan in their aforementioned article. It consisted essentially of a bell of earthenware containing the gas carbon anode, and having its mouth covered by the diaphragm which was in contact with the anode, and was held in place by iron wire gauze forming the cathode of the cell. The whole was placed in an iron tank containing saturated brine and the bell was filled with brine to a level above that of the cathode compartment. The electrodes were close together,

and the internal resistance of the cell was small. The carbon anode was produced from large pieces of gas carbon imbedded in lead at one end above the liquid, and usually packed with smaller pieces of carbon, so as to give a large anode surface in contact with the diaphragm (see Figs. 2, 3, and 4). The iron

FIG. 2.

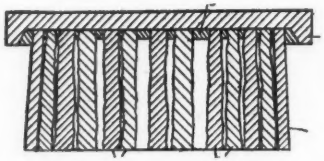

FIG. 3.

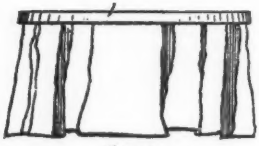

FIG. 4.

wire gauze forming the cathode was never in contact with the chlorine gas, and was so little acted upon by the caustic soda solution that it was one of the most permanent parts of the cell. This is also true of the iron tanks containing the cells and caustic solution. The diaphragm consisted of asbestos and had to be renewed every few weeks. This diaphragm was by no means expected to entirely prevent all diffusion of sodium hydroxide into the anode compartment nor of some hypochlorite in the reverse direction, but it did largely prevent the two solutions from mixing. Such a cell gave a working efficiency of about seventy per cent. and could be worked with an electromotive force of about four volts. It was soon found that the earthenware bell was not a practical form of apparatus, as they were easily broken, and even cracked by change of temperature. Consequently a new form of covering was devised, made from slate, with a spruce frame, which came in contact with the

caustic solution only, and was little effected thereby. The essential features of the process remain the same.

On passing the current reactions took place much as described by Oettel,[1] the main one being the electrolysis of sodium chloride, forming sodium and chlorine, the sodium immediately attacking the water in the cathode compartment, giving off hydrogen and leaving sodium hydroxide in solution. The chief difficulty of the process has always been to keep the sodium hydroxide in its proper compartment, for with the very best of diaphragms a limited amount of diffusion into the anode compartment will take place. Secondary reactions at once set in between any diffused sodium hydroxide and the chlorine present, forming sodium hypochlorite, which in turn will partially diffuse into the outer space and, contrary to Oettel's experience, is not reduced at the cathode, but is oxidized to sodium chlorate either before diffusion or during the evaporation of the cathode solution, and is eventually recovered as a by-product in the form of potassium chlorate. Besides the formation of hypochlorite, the diffusing sodium hydroxide is itself partially electrolyzed and the oxygen produced will immediately attack the carbon of the anode, very much complicating matters by forming carbon dioxide. The electrolysis of sodium hypochlorite will also give rise to nascent oxygen and increase the amount of carbon dioxide produced. This formation of carbon dioxide is a very serious matter in the production of bleaching powder, for unless removed from the chlorine gas it renders impossible the manufacture of a standard grade. The carbon anodes may be graphitized, rendering them much more resistant, but this difficulty is entirely eradicated when platinum is used. All of the reactions taking place in the anode compartment have been, without reference to the diaphragm, largely reduced by two patents of Le Sueur, which have broadly protected features that are, in my opinion, essential to the successful production of sodium hydroxide and chlorine by any method electrolyzing salt solution and using a diaphragm. The first of these is to have the liquid of the anode compartment at a higher level than that of the cathode, thus diminishing the entrance of sodium hydroxide by diffusion; and the second is to add hydrochloric acid to

[1] *Chem. Ztg.*, *1894*. pp. 18 and 69.

the anode compartment so as to keep the solution slightly acid. This hydrochloric acid so added at once decomposes any hypochlorite, and is itself oxidized so that all of its chlorine is regained in the form of that gas. No chlorine is lost by this operation, for the chlorine obtained as bleaching powder is just so much greater than the equivalent of the sodium hydroxide as the amount of chlorine in the hydrochloric acid added. To the Electro Chemical Company this use of hydrochloric acid is a matter of some expense, for an equivalent of chlorine at Rumford Falls costs a little more in the form of hydrochloric acid than it is worth in bleaching powder. It will readily be seen, however, that in other localities and, especially near Le Blanc soda factories, the use of hydrochloric acid would be a positive advantage from a standpoint of economy.

The Le Sueur cell at present in operation at Rumford Falls embodies all the essential features which I have outlined, but it is larger, simpler of construction, and the carbon anode has at last been discarded in favor of a special form of platinum anode recently invented by Le Sueur. The cell as now used (Fig. 5)

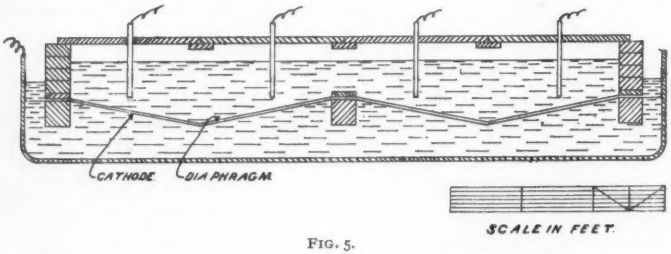

FIG. 5.

is contained in a tank five by nine feet and one and one-half feet deep, and made of one-quarter inch boiler steel. Excepting the asbestos, which composes the diaphragm, the wire netting of the cathode, and the materials of the positive electrode, it is built entirely of spruce, red brick, Portland cement, sand, and slate. These substances are so disposed in the cell as to be practically permanent, the wood being exposed to no action except that of the caustic solution, which has little effect upon it. The anodes are introduced from the top of the cell and may be removed singly without interrupting the process. Troublesome

joints are closed with a specially prepared plastic cement. The diaphragm is tipped somewhat from the horizontal for the purpose of permitting the easy egress of the hydrogen bubbles. The foundation of the cell within the tank consists of an oblong frame of spruce, eight feet four inches by four feet ten inches, outside measurement, and eight inches less on both dimensions inside. This frame is eleven inches deep, only the side pieces, however, resting upon the floor of the tank. The end pieces consist of four four-inch timbers whose upper surfaces are ten inches above the floor of the tank and one inch below the top surface of the longer side. The frame is divided transversely by a timber, similar to each of the end timbers, which crosses the middle of the frame at the same level as the end pieces. This center beam forms a bridge over which the flat iron ribs supporting the cathode are hung. The cell is thus divided into two equal spaces merely for mechanical convenience. The ribs referred to consist of four parallel pieces of flat iron, three of them being one and one-half by three-eighths inch, and the fourth, twice as wide. This wider piece is fastened at both ends to the containing tank, so as to receive from the latter the electric current which enters through the material of the tank and communicates the current to the cathode which rests upon these iron ribs. The diaphragm rests directly upon the cathode. The depth of the trough formed by the slanting ribs is four inches. There is an adequate arrangement at the ends of the bridge pieces by means of which the hydrogen, finding its way to this higher level, is delivered to exit pipes communicating with the atmosphere or with any system of piping to which it is desired to deliver it. The inch of space between the tops of the cross timbers and the side pieces is utilized to take a piece of slate four feet long by four inches wide by one inch thick. This presses down upon the diaphragm and the cathode netting and keeps all solid. On top of the sides and ends of the frame there are four courses of common brick laid in clear cement. There is a coating of cement applied to the inside walls of the portion of the cell forming the anode compartment, and this includes not only the brick walls, but the small portion of the wooden sides above the cathode which would otherwise come in contact with the anode liquid. The ceiling of the cell consists simply of pieces of slate

two feet by one foot, and suitably supported by transverse strips of slate one inch thick by four inches wide. Through the ceiling plates pass the glass tubes to which the anodes are attached.

The anodes which are now used are made from an alloy of iridium and platinum, and are so constructed that a very large anode surface is presented at an almost incredibly small cost when it is considered that it is not at all of the nature of a plated surface, but is an anode of solid metal. Sixty anodes on an average are used to each cell, and each anode costs seventy-three cents at the present market price of platinum. They are acted upon chemically but slightly if at all. If the glass holders break there is no loss of platinum and a new anode can immediately be put in place. The total cost for the anodes of a plant producing, per month, 200 tons of bleaching powder, is approximately $5,000, or $40 for a cell producing fifty-five pounds of sodium hydroxide and fifty pounds of chlorine per day; and this allows for a very low cell efficiency. The total cost for the renewal of the platinum, including labor, is less than half the cost of the bare carbon alone as it was formerly used. Besides, it must be remembered that carbon anodes are certain to give more or less carbon dioxide if hypochlorite be present, while with these iridio-platinum anodes no carbon dioxide can possibly be produced.

At Rumford Falls, the Electro-Chemical Company obtains power at a very low cost, so that it pays to obtain a maximum of work from each cell by using a higher current density in proportion to the anode surface than might be tenable under other conditions. As the cells are now constructed, a current of 1,000 amperes is passed through each cell under a pressure of six and one-half volts. I am aware that this voltage is high, and from a statement in Lunge,[1] he would probably, at first thought, condemn the process on this ground alone. But it will readily be understood how this increased voltage can be economically employed when it is considered that at $8.00 per electrical horse power per year, which is the cost of power to the company at Rumford Falls, the extra cost per pound of product, on an average efficiency of eighty per cent., is but $0.00015 for each extra volt used. This high voltage is, by no means, an essential of the

[1] Alkali Industry, Vol. III.

process, and each cell can be run on a lower amperage when, of course, less pressure would be required. It is simply a fact that, at Rumford Falls, it is economical to run the cells on this voltage, forcing through them all the current they can take without undue heating. Under these conditions, the renewal of the cell is usually made necessary only on account of the deterioration of the diaphragm. The diaphragms have an average life of seven weeks, and have been used twenty-four consecutive weeks without renewal. The cathodes are but little acted upon, and the steel tanks are practically indestructible.

The cells are arranged so that twenty-two are in series, and three series are run in parallel on two dynamos. The hydrogen is used only for working platinum, the larger part being allowed to escape into the atmosphere. The chlorine is conducted by earthenware pipes to lead chambers and absorbed by lime in the usual manner, although, at present, a part is used for the manufacture of potassium chlorate. The caustic solution is concentrated by evaporation *in vacuo* and is separated from the major part of the undecomposed salt by centrifugals. Any chlorate is now readily removed, and the solution is then boiled down in cast-iron kettles to a first quality caustic soda analyzing about seventy-four per cent. sodium oxide. The recovered salt is converted into brine and is used in the cathode compartment of the cells,—nothing but fresh brine and some hydrochloric acid being ever added to the anode side. Whole bays of twenty-two cells have shown daily averages of over ninety per cent. chlorine efficiency, and weekly averages of eighty-seven per cent. If the anode compartment could be kept constantly acid, as can be done with single cells, a chlorine efficiency approaching very closely to the theoretical may be reached. The efficiency reckoned upon the sodium hydroxide produced is not quite so high.

One great field for electrolytic processes is the production of bleaching liquors and caustic solutions for bleacheries, paper mills, and the like. Large economies might be introduced by companies of this kind by making their own solutions electrolytically instead of by the usual method of first transporting the chlorine in the form of bleaching powder and the alkali in the solid state. This is almost self evident when one considers that

the final evaporation of the caustic soda, which is quite costly, is done solely for purposes of transportation; that the absorption of chlorine by milk of lime is a very simple operation, and the bleach liquors, so produced, are much more efficient per unit of chlorine than bleaching powder; and that the raw material, salt, is easily and cheaply obtained and transported without deterioration, while a small plant can be run almost as economically as a large one. In fact, the Electro-Chemical Company has sold a great deal of chlorine in the form of bleach liquors to pulp mills, at reasonable distances from the works, that preferred to take this liquid carrier of chlorine on account of its ready settled solution, ease of manipulation, and its greater efficiency, although the cost of transportation might be somewhat greater. In works which do not require caustic soda the process would also be highly economical for under such conditions the cathode liquor can be directly used to absorb the chlorine, in excellent condition for bleaching purposes, thus doing away entirely with the cost and use of lime. I do not hesitate to predict that we shall yet see many Le Sueur plants established in connection with mills now using bleaching powder. In fact one of our largest American sulphite pulp mills has already made arrangements for a trial of the Le Sueur plant with the view of bleaching to a very large extent.

In closing, allow me to call your attention to the fact that any process for the production of caustic soda and bleaching powder has had to struggle under great difficulties during the last six years on account of the tremendous fall in the market price of those commodities, and without great inherent merit no electrolytic process could have survived its infancy. This fall in price has been due to the vigorous competition of the alkali industries of England and of Germany, and of increased home production, rather than from any improvement of old methods, or from the establishment of new processes. The fact that both England and Germany have a freer market in this country to-day than they had when the first electrolytic process was introduced, is also, in part, responsible for the fall in price. In 1892, when the plant at Rumford Falls was built, bleaching powder sold in Boston for $45.00 per ton, and caustic soda for $74.00

per ton. The prices to-day are $30.00 and $36.00 respectively. The fall in price of products here shown is equivalent to eighty per cent. of the present total gross income, and means that any surviving process must have reduced, not only its operating expenses, but also its profits. It is not at all surprising that under such adverse conditions many electrolytic methods have failed commercially.

The question of cost of production is one of prime interest to the alkali manufacturer, but depends very largely upon location, and upon cost of power. In the following estimate prices are given which are liberal for Western New York, where cheap power may be obtained. Salt, in the form of brine, and lime might be procured in other places much cheaper, and allowance is made for a much larger amount of hydrochloric acid than is now used. Where power is provided in the form of electricity, as at Niagara Falls, there is no cost for power installation.

Cost of plant for producing 20,000 pounds prime bleaching powder and 7,000 pounds caustic soda per day would be, exclusive of power and generator installation, $60,000.

DAILY OUTLAY.

Salt, 13,000 pounds (at $2.50 per ton laid down)	$16.25
Lime, 10,000 pounds (at $5.00 per ton laid down)	25.00
Muriatic acid (2,000 pounds hydrochloric acid)	20.00
Coal (for evaporating, and incidentally generating 250 H. P. of the total power required), seven gross tons at $3.00	21.00
Labor, forty-five men, at average of $1.60	72.00
Superintendence and bookkeeping	7.50
Packages	15.00
Oil, waste, and sundries	10.00
Taxes and insurance	5.00
Repairs and sinking fund	25.00
Miscellaneous	5.00
Power, 1,000 H. P. (at $12.00 per E. H. P. year)	33.00
Total daily cost	$254.75

DAILY OUTPUT.

20,000 pounds bleaching powder, at 1½ cents	$300.00
7,000 pounds caustic soda, at 1½ cents	105.00
	405.00
Less freight to market and commission	55.00
Total daily income	$360.00

Local conditions effecting cost of raw material, freight, and power, and changes in market price of product, would greatly influence the value of this estimate. With these figures, however, any one may readily calculate the probable cost in any locality when the conditions affecting it are known.

NEW HAMPSHIRE COLLEGE,
DURHAM, N. H.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CASE SCHOOL OF APPLIED SCIENCE.]

COMPOSITION OF OHIO WINES.

BY ALBERT W. SMITH AND NORMAN PARKS.

Received September 2, 1898.

NORTHERN Ohio is one of the most important grape-growing regions in the United States, and produces no inconsiderable quantity of wine from the yearly growth, but, so far as we are aware, no systematic study of the chemical composition of these wines has ever been undertaken. In order to determine whether a sample of wine is pure or not, it is often necessary to know what is the average chemical composition of samples of guaranteed purity, made from the same kind of fruit and grown in the same region. An examination of a large number of Ohio wines, bought in this market, showed a considerable variation in composition from the average of French, German, and California wines. It was thought desirable to ascertain if this was due to a very universal sophistication of Ohio-made wines in this market, or whether it was due to an actual difference in the nature of the fruit grown here, or possibly in the method of manufacture and fermentation.

In the fall of 1894, and of 1895, samples of most of the prominent varieties of Ohio grapes were collected, the juice expressed

and converted into wine according to the manner generally practiced in this locality. Both seasons were favorable to the growth of fine fruit, and, as nearly as possible, an average quality of each sample was selected. In every case the fruit was mature and fully ripened when gathered. No fermentation was allowed to take place between the times of grinding and the pressing of the juice from pulp and stems.

Fermentation was carried on in jugs, at the temperature of the outside air, until freezing weather, when the jugs were placed in a cool cellar until February. The wine was then carefully siphoned into bottles and further fermentation arrested by Pasteurizing at 160° F. The bottles were then corked and stored until wanted for analysis. In all cases except two, the samples were about one year old when analyzed. The samples made from Concord and Catawba grapes were two years old. The methods of analysis used were those published in Bulletin 43, U. S. Department of Agriculture, Division of Chemistry.

The results are expressed in Table I as grams per 100 grams of wine, or per cent. by weight. In Table II are the results of analyses of a number of typical samples of wine sold in the markets of Northern Ohio.

Comparing the results of analyses of these twelve samples of pure wines with those of European origin, made from similar fruit,[1] it is noticeable that gravity, acidity, and proportion of alcohol, potassium acid tartrate, and tartaric acid are quite similar. The average of solids in the Ohio samples is slightly lower than that of the foreign-grown wines. These latter contain usually somewhat more than two per cent., though individual cases occur which fall below this limit.

The most important differences are in the percentages of glycerol and ash. Published reports of European samples indicate the ash usually above two-tenths per cent. and from five-tenths to eight-tenths per cent. glycerol, while the maximum and minimum for those analyzed here are 0.15 and 0.10 for ash, and 0.95 and 0.29 per cent. respectively, for glycerol.

Since these two constituents, together with the solids, are of most importance and general use in determining the genuine-

[1] Fresenius: *Ztschr. anal. Chem.*, 36, 413.

TABLE I.

Variety of grapes.	Grams per 100 grams wine.											
	Concord.	Ives.	Hayse.	Catawba No. 1.	Centennial.	Werden.	Hartford.	Delaware.	Riesling.	Niagara.	Catawba No. 2.	Catawba No. 3.
Specific gravity	0.9921	0.9971	0.9959	1.0010	0.9934	0.9970	0.9977	0.9909	1.0060	0.9931	0.9918	0.9972
Total acid as acetate	0.27	0.29	0.23	0.32	0.30	0.36	0.91	0.30	1.46	0.26	0.26	0.37
Alcohol	12.0	8.45	7.90	10.5	8.20	7.40	5.10	11.5	3.30	8.77	11.4	8.82
Glycerol	0.55	0.42	0.36	0.51	0.40	0.42	0.29	0.45	0.39	0.50	0.50	0.95
Solids	1.93	1.61	1.51	3.66	1.28	1.81	1.55	1.65	2.29	1.58	2.00	3.86
Ash	0.14	0.14	0.14	0.15	0.11	0.13	0.15	0.12	0.12	0.10	0.12	0.12
Phosphoric anhydride	0.004	0.005	0.008	0.003	0.001	0.009	0.003	0.005	0.004	0.007	0.005	0.008
Sugar	0.11	0.12	0.11	1.54	0.11	0.92	0.12	0.10	0.10	0.11	0.07	...
Nitrogen	0.007	0.009	0.008	0.007	0.005	0.011	0.005	0.017	0.008	0.008	0.013	...
Volatile acid as acetic	...	...	...	0.031	0.20	0.11	0.12	0.07	...	0.12	0.21	0.30
Potassium bitartrate	0.31	0.28	0.40	0.30	0.23	0.24	0.31	0.24	0.20	0.16	0.25	0.20
Free tartaric acid	0.05	0.10	0.12	0.11	0.08	0.09	0.10	0.08	0.07	0.05	0.03	0.05
Tannin	0.04	...	...	0.04	0.02	0.03	0.03	0.03	0.02	0.02	0.02	0.03
Glycerol as parts per 100 parts alcohol	4.5	4.8	4.6	4.9	4.8	5.7	5.7	3.9	11.8	5.6	4.4	10.7

TABLE II.

Kind.	Grams per 100 grams wine. Solids.	Alcohol.	Ash.	Acid as tartaric.	Glycerol.	Reducing sugar.	Sucrose.	Volatile acid as acetic.
Sour Catawba.....	1.42	8.19	0.20	.0.45	0.57	0.15	none	0.30
" "	1.42	11.95	0.16	0.22	0.51	0.18	none	0.45
" "	1.54	9.86	0.15	0.27	0.57	0.14	none	0.20
" "	1.59	15.65	0.09	0.45	0.45	0.26	none	0.32
" "	1.45	10.24	0.24	0.30	0.38	0.20	none	0.20
" "	2.26	10.57	0.14	0 27	0.37	0.28	none	0.30
" "	1.75	9.24	0.10	0.20	0.27	0.25	none	0.17
" "	1.36	10.45	0.13	0.48	0.48	0.30	none	0.33
Sweet Catawba....	13.7	20.20	0.40	0.38	0.33	13.00	none	0.31
" "	14.0	13.80	0.27	0.23	0.46	12.7	none	0.19
" "	16.9	12.10	0.15	...	...	16.4	none	0.20
" "	15.9	9.80	0.15	...	...	14.2	none	...
" "	18.9	9.07	0.17	...	0.17	14.5	0.90	...
" "	15.0	9.92	0.21	...	0.24	13.6	none	...
Port Wine.....	14.8	19.3	0.20	0.15	0.28	14.7	none	...
" "	20.3	8.92	0.19	...	0.49	15.4	1.47	...
" "	10.8	18.7	0.24	...	0.31	9.1	none	...
California Port ...	11.6	16.7	0.30	...	0.39	13.2	none	...
" " ...	13.11	16.9	0.25	0.30	0.30	...	none	...
Old Angelica.....	15.1	17.3	...	0.25	0.31	14.2	none	...
Sherry	4.71	13.8	0.31	...	0.45	3.1	none	...
Niersteiner.....	1.57	9.29	0.22	0.30	0.97	...	none	...
Muscatel	16.2	17.2	0.22	0.08	0.09	...	none	...
"	15.1	20.7	0.21	0.20	0.33	13.2	none	...

ness and purity of a sample of wine, these differences are most important. Most authorities state that, in the natural process of alcoholic fermentation, glycerol and alcohol are produced in the ratio of from 7 to 14 parts of the former to 100 parts of the latter. If this be always true, the inference to be drawn, when this maximum is exceeded, is that glycerol has been added, while in case the ratio of glycerol to alcohol is below 7 : 100, that the sample has been fortified by the addition of alcohol foreign to the product of fermentation. Such conclusions in the case of these Ohio wines would be quite misleading. In the same manner, care must be exercised, when these wines are under considera-

tion, in drawing conclusions as to the addition of water, from the facts of low ash and solids.

The skilful adulteration of wine is extremely difficult to detect by chemical analyses, and these abnormally low results, obtained by analysis of perfectly pure and reliable samples, make such conclusions from these determinations all the more unsatisfactory.

It is of interest also to compare the composition of these samples with that of authentically pure California samples. Many such analyses have been made and reported by Prof. Hilgard,[1] and while they do not include determinations of glycerol, the contents of ash and solids are usually higher than those of European samples.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 3.]

THE DETERMINATION OF SULPHUR IN ASPHALT.

BY E. H. HODGSON.

Received September 22, 1898.

THE numerous articles recently published on the analysis and chemistry of asphalts, and the wide range of opinion as to the relative values of the different methods in use for the determination of sulphur, have led me to make a comparison of results on some typical asphalts.

Dr. E. H. Miller, through the kindness of Mr. A. W. Dow, of Washington, was enabled to secure samples, the sources and natures of which were known. The samples were labeled Trinidad Lake, Trinidad Crude, Trinidad Lake Refined, Cuban Crude, Alcatraz Crude, and California Crude, and were described by Mr. Dow as follows:

Trinidad Lake.—Asphalt from the lake on the island of Trinidad, imported by Barber Asphalt Co. for paving.

Trinidad Crude.—Crude asphalt from Hadley's Diggings, about one mile from Trinidad Lake. It is known as "iron pitch," being the hardest asphalt found in Trinidad.

Trinidad Lake Refined. This is crude Trinidad Lake asphalt, melted up to drive out the water.

Alcatraz Crude.—From Ventura Co., California, used by

[1] Bulletin 13, Division of Chemistry, U. S. Department of Agriculture.

the Alcatraz Asphalt Co. for paving, after the addition of liquid asphalt.

California Crude.—From Kern Co., California, used by the Standard California Asphalt Co. for paving, after the addition of liquid asphalt.

Sample "Trinidad Lake" was found to lose water very rapidly, so it was heated to about 60° C. (not sufficient to melt it) and then remained constant.

The samples were ground as fine as possible in a mortar, and then placed in glass bottles, fitted with tight corks. From these bottles average samples were taken and kept in test-tubes for use.

HEATING WITH STRONG NITRIC ACID IN A SEALED TUBE—CARIUS' METHOD.

The tubes were made in the usual way from heavy glass tubing. Two determinations were made on each sample. One on one-half gram and one on three-fourths gram. A general description of the method is as follows: One-half gram of asphalt is introduced into the bottom of the tube, and fifteen cc. of fuming nitric acid (1.60 sp. gr.) is poured upon it. The open end of the tube is then drawn out into a thick-walled fine-caliber tube, but not sealed. The tube is then heated, for about six hours, in a water-bath kept at 80°–90° C. Then five cc. more acid are added, the tube is sealed, and heated in a guarded furnace at a temperature of about 150° C. for from four to five hours. Allow the tube to cool, then open and reseal, and reheat for from two to four hours at a temperature of 180°–200° C. Cool, open, and remove the liquid and residue into a No. 2 beaker. Dilute with water, filter, and wash. If the residue contains anything but sand it is saved and treated separately. The filtrate is evaporated to dryness on the water-bath, adding a piece of solid sodium hydroxide. The nitric acid is driven out by repeated evaporation of the solution, with the addition of hydrochloric acid, and the silica dehydrated in an air-bath at 110°–115° C. Cool the dehydrated mass, add two to three cc. of hydrochloric acid and 100 cc. of water, stir well, filter, and wash well with hot water. Dilute the filtrate to about 200 cc., heat to boiling and while boiling add twenty cc. of barium chloride (twenty per cent. solution), drop by drop, from a burette, at the rate of

about a drop a second. Stir all the time. Boil the solution about ten minutes, and allow it to stand twenty-four hours. Filter, wash with hot water, and ignite. Treat with sulphuric acid and reignite. Then cool and weigh the barium sulphate. A pure white product was obtained, and the precipitate did not run through the filter.

The residue from the sealed tube, if not thoroughly oxidized, is fused with six grams of mixed carbonates and one gram of potassium nitrate. The fusion is dissolved in water and hydrochloric acid. The nitrates are destroyed by evaporating with the addition of hydrochloric acid, and the silica dehydrated as before. Filter off the silica and wash. Then determine the sulphuric acid in the filtrate as before described.

When three-fourths gram of asphalt was used, twenty-five cc. of fuming nitric acid were employed instead of twenty cc.

The following results were obtained :

	Weight of barium sulphate. Gram.	Sulphur. Per cent.
Trinidad Lake.		
One-half gram	0.1526	4.192
Residue	0.0051	0.140
		4.332
Three-fourths gram	0.2238	4.10
Residue	0.0068	0.18
		4.28
Trinidad Crude.		
One-half gram	0.1249	3.400
Residue	0.0034	0.086
		3.486
Three-fourths gram	0.1720	3.148
Residue	0.0106	0.19
		3.338
Trinidad Lake Refined.		
One-half gram	0.1585	4 35
Residue	....	....
		4.35

	Weight of barium sulphate. Gram.	Sulphur. Per cent.
Three-fourths gram	0.2160	4.21
Residue	0.0137	0.25
		4.46
CUBAN CRUDE.		
One-half gram	0.1315	3.61
Residue	....	....
		3.61
Three-fourths gram	No results.	
ALCATRAZ CRUDE.		
One-half gram	0.1839	5.05
Residue	0.0195	0.54
		5.59
Three-fourths gram	0.2749	5.12
Residue	0.0294	0.46
		5.58
CALIFORNIA CRUDE.		
One-half gram	0.2589	7.11
Residue	0.0145	0.398
Three-fourths gram	No results.	

DEFLAGRATION METHOD—S. F. AND H. E. PECKHAM.

A porcelain crucible is heated to a dull red heat, and *small* amounts of a mixture of one gram finely ground asphalt, eight grams of potassium nitrate, and eight grams of mixed sodium and potassium carbonates, added from time to time, just keeping the material in the crucible melted. When all of the mixture has been added, heat to perfect fusion with a blast-lamp, and cool. Dissolve the fusion in twenty cc. hydrochloric acid and forty cc. of water, and wash the crucible well with hot water. The solution is evaporated down to dryness, dehydrated at 110°–115°, the silica filtered off, and the sulphuric acid determined in the filtrate as before. The results are as follows:

TRINIDAD LAKE.

No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1	0.2770	3.804
2	0.2689	3.68

TRINIDAD CRUDE.

No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1	0.2443	3.37
2	0.2359	3.24
TRINIDAD LAKE REFINED.		
1	0.2634	3.62
2	....	....
CUBAN CRUDE.		
1	0.2009	2.76
2	0.2052	2.82
ALCATRAZ CRUDE.		
1	0.3054	4.19
2	0.2773	3.81
CALIFORNIA CRUDE.		
1	0.4376	6.50
2	....	....

SODIUM PEROXIDE METHOD.

Place one gram of the fine asphalt in the bottom of à large nickel crucible. Cover with a layer of about four grams of mixed carbonates and about one gram of solid sodium hydroxide. Cover the crucible and heat gently until the gases are driven off. Then raise the heat and add small amounts of sodium peroxide, from time to time, until no further action is noticed on the addition of fresh Na_2O_2. Then, with the blast-lamp, heat to perfect fusion. This takes but a few minutes. Pour as much of the fusion as possible upon the cover of the crucible and cool slowly. Place the fusion, crucible, and cover in a casserole containing fifty cc. hot water, and after thorough digestion on the water-bath, filter off the residue, and wash well with hot water. The filtrate is made acid with hydrochloric acid, and evaporated down to dryness, dehydrated at 110°–115° C., the silica filtered off, and the sulphuric acid determined in the filtrate as already described. Results by this method:

TRINIDAD LAKE.

No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1	0.2687	3.69
2	0.2744	3.77

TRINIDAD CRUDE.

No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1	0.2426	3.33
2	0.2360	3.25
TRINIDAD LAKE REFINED.		
1	0.2962	4.07
2	0.2929	4.02
CUBAN CRUDE.		
1	0.2256	3.10
2	0.2230	3.06
ALCATRAZ CRUDE.		
1	0.2887	3.97
2	0.2880	3.96
CALIFORNIA CRUDE.		
1	0.4557	6.26
2	0.4481	6.15

IGNITION WITH CALCINED MAGNESIA—ESCHKA'S METHOD.

One gram of finely ground asphalt is intimately mixed with one gram of calcined magnesia and about one-half gram of dry mixed carbonates is added. Mix well and place in a platinum or porcelain crucible. With the crucible in an inclined position, heat at a dull red heat, stirring every few minutes until the ash is a dull yellow. Cool and add about one gram of finely ground ammonium nitrate and mix thoroughly. Heat slowly to a dull red, and continue the heating until the ammonium nitrate is entirely decomposed. Cool, extract the mass thoroughly with water (hot water preferred), filter, and wash well. Acidulate the filtrate with hydrochloric acid, and precipitate the sulphuric acid as before described. The results are as follows:

TRINIDAD LAKE.

No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1	0.2660	3.65
2	0.2791	3.83
TRINIDAD CRUDE.		
1	0.2608	3.58
2	0.2567	3.53

TRINIDAD LAKE REFINED.

No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1	0.2744	3.77
2	0.2650	3.64

CUBAN CRUDE.

1	0.2020	2.77
2	0.1941	2.66

ALCATRAZ CRUDE.

1	0.3054	4.19
2	0.3021	4.16

CALIFORNIA CRUDE.

1	0.5011	6.88
2	0.5109	7.01

The relative accuracy of the different methods is best shown by tabulating the results, as follows:

	Trinidad Lake.	Trinidad Crude.	Trinidad Lake Refined.	Cuban Crude.	Alcatraz Crude.	California Crude.
Sealed tube	4.33	3.49	4.35	3.61	5.59	7.51
	4.28	3.34	4.46	...	5.57	...
Deflagration	3.80	3 37	3.62	2.82	4.19	6.50
	3.68	3.24	...	2.76	3.81	...
Peroxide	3.69	3.33	4.07	3.10	3.97	6.26
	3.77	3.25	4.02	3.06	3.96	6.15
Eschka's	3.65	3.58	3.77	2.77	4.19	6.88
	3.83	3.53	3.64	2.66	4.16	7.01

It would appear, therefore, that the "sealed tube" gives the most accurate results, but on account of the explosion of the tubes and the time required for a determination, it would probably be barred out.

The deflagration method apparently gives low results. It is much shorter than the sealed tube, but longer than either the peroxide or Eschka's method.

Of the latter two, the Eschka's method is perhaps the better, as it requires less time and attention to carry out, and gives about as good results.

The peroxide method is shorter than the deflagration method and about as accurate.

The reagents employed were first tested for sulphur.

	Sulphur. Per cent.
The sodium and potassium carbonate contained.....	0.005
The sodium peroxide contained.....	0.003

The rest of the reagents were sulphur free or contained but the merest trace.

NOTE.

Testing for a Yellow Azo-Color in Fats, Etc.—In this Journal, 20, 110, Joseph F. Geissler describes a delicate test for the detection of a yellow azo-dye used in coloring fats. The test has proved of the greatest service to me, and I make use of it constantly. While experimenting upon the subject, I have noted another simple test for this azo-color that seems fully as delicate as Geissler's. To a few cubic centimeters of the pure filtered fat in a large test-tube are added an equal volume of a mixture of one part strong sulphuric acid, and four parts glacial acetic acid. The contents of the tube are then heated almost to boiling, and thoroughly mixed by violently agitating the bottom of the tube. When now allowed to stand and separate, the lower layer of mixed acids will be strongly colored wine-red if the azo-color be present. Pure butter-fat imparts no color, or at most only a very faint brownish tinge to the acids. Strong hydrochloric acid may replace the sulphuric in the above mixture, or a mixture of one part strong sulphuric acid, and three parts water may be used, but I have obtained the best results in the manner described.

ALBERT H. LOW.

DENVER, COLORADO, August 27, 1898.

NEW BOOKS.

A BRIEF COURSE IN QUALITATIVE ANALYSIS. BY ERNEST A. CONGDON, PH.B., F.C.S. New York: Henry Holt & Co. 1898. iv + 62 pp. Price 60 cents.

Professor Congdon has given us a very satisfactory little text-book. While brief, the course, so far as it goes, is quite thorough.

The arrangement of the book is excellent and the selection of matter carefully made. Blank leaves for notes are inserted between the pages. The classification of the metals into groups for the purpose of analysis is first shown. Then the reactions of the metals are given. Following the single reactions of each group is given the method of analysis for the group. In most cases an alternative scheme is also printed. A notable exception is in the case of the barium group where the writer gives only the separation of strontium from barium, depending on the different solubilities of their nitrates in absolute alcohol. The reactions of the acids follow those of the metals. The order is alphabetical and not according to groups. The scheme for the detection of iodides, chlorides, and bromides, where more than one is present, by separate tests for each, does not commend itself to the reviewer, and might well be substituted by Professor Hart's easier and simpler method. The section on the treatment of solids is clearer and more concise than that given in most small books. Throughout the book the aim of the writer seems to have been to make the student think. This is borne out by the notes which follow the analytical schemes and by the table of solubilities and list of questions which close the book.

RICHARD K. MEADE.

ALKALOIDAL ESTIMATION; A BIBLIOGRAPHICAL INDEX OF CHEMICAL RESEARCH PREPARED FROM ORIGINAL LITERATURE FOR THE COMMITTEE OF REVISION. BY PAUL I. MURRILL, under the direction of ALBERT B. PRESCOTT. Ann Arbor, 1898. "Published by the Committee of Revision" of the Pharmacopoeia of the United States of America, 1890–1900. Not for sale.

This is a pamphlet of 58 pages "in boards," and embraces the easily found work upon its title subject from 1861 to 1898. It consists entirely of clerical labor very well done and its arrangement is convenient for reference.

The contents are first a list of the more important of the series of publications examined, and then an alphabetical list of other periodicals to which references are given. Then the body of the work is in three parts.

Part I is the chronological index where, in giving the references, original papers are first given. Then republications and abstracts; and the abbreviations used are, as far as practicable, those of Bolton's "Bibliography of Chemistry."

Part II is an alphabetical index of authors referred to with dates and reference numbers to the dates in Part I.

Part III is a subject index where a similar arrangement of dates and numbers are used, the subject coming first in alphabetical order, and the name of the author last.

On pages 10, 11, and 12, are given the full text of the assay processes of the British Pharmacopoeia of 1885 for cinchona, nux vomica, and opium, and on pages 38, 39, and 40, are given the full text of the assay processes of the same Pharmacopoeia of 1898 for belladonna, cinchona, ipecac, nux vomica and opium tincture.

On pages 33 and 34, are given a translation of the assay processes of the German Pharmacopoeia of 1895 for cinchona and opium, and on pages 22, 23, 24, 25, and 26, are given the assay processes of the U. S. Pharmacopoeia of 1890 for cinchona, nux vomica, and opium.

The recent British Pharmacopoeia gives also an assay process for opium which is not quoted here apparently because it is so nearly identical with the process for making the tincture of opium by assay. But it would have been better to have quoted the process for opium rather than that for the tincture, since it is very convenient to have all the complete pharmacopoeial processes quoted here together for ready reference in accordance with the general plan of the pamphlet.

The chief utility of this work outside of the Committee of Revision, is in the time and labor that may be saved by it to any one who is about to undertake any research or investigation of any of the natural alkaloids, and although its field is not large it is rather to be regretted that the "pamphlet is not for sale." It is however altogether probable that any one needing a copy may get it from the committee.

E. R. SQUIBB.

TRAITÉ D'ANALYSE DES SUBSTANCES MINÉRALES. PAR A. CARNOT. Tome premier.—Méthodes Générales d'Analyse Qualitative et Quantitative. Paris: V^ve^ Ch. Dunod, Editeur. 1898. 992 pp.

This treatise on mineral analysis by M. Carnot is to consist of three volumes of about 1000 pages each. The first volume which has just been issued comprises 992 pages of which 459 are devoted to qualitative methods.

The first chapter treats of the blowpipe and blowpipe methods including heating in open and closed tubes, on charcoal and on the end of a platinum wire; flame reactions and fusion in borax and microcosmic-salt beads; fusion with sodium carbonate, with reagents on charcoal and on platinum foil; the tests for sulphur and examination with cobalt solution. The separation and distinctive tests for the metals are given tersely and clearly.

Chapter 2 treats of the Bunsen burner, and contains a scheme for the systematic examination of a sample by the previously described methods.

Chapter 3 treats of the spectroscope and accessories.

Chapter 4 takes up microchemical examinations and is an extremely interesting and instructive essay on this subject containing as it does much of the original work of the author.

Chapters 5, 6, and 7 comprise the wet methods of qualitative chemical analysis, the characteristic reactions of the bases and acids of the various elements, and the methods for making and purifying the reagents employed in chemical analysis.

It is difficult to say too much in praise of this part of the work. The scheme for the systematic qualitative examination of an unknown substance is admirably described. The language is clear and intelligible and the explanations lucid without diffuseness. What are usually considered the rare elements are treated as fully as those of more common occurrence, constituting a marked difference between this work and nearly all others on qualitative analysis, and giving it a value decidedly exceptional.

With chapter 8 begins the operations employed in quantitative analysis and includes sampling, pulverizing, drying, and weighing.

Chapter 9 gives operations in the dry way; descriptions of furnaces, crucibles, etc.; fusion and fluxes. Fletcher's gas furnaces and burners are not mentioned, although in my opinion they are superior to any of those described.

Chapter 10 describes methods in the wet way. General operations including solution, evaporation, distillation and the precipitation, filtration, washing, drying, burning, and weighing of precipitates. In the description of filtering apparatus no reference is made to the Gooch crucible which to analysts in America must appear a serious omission.

Chapter 11 treats of the apparatus and general principles involved in the determination of metals by electrolysis. From the historical résumé it appears that Davy in 1808 was the first to deposit a metal by the aid of the current, he having obtained potassium in an amalgam, from potassium hydrate, and Luckow in 1869 was the first to employ electrolysis as a method for the determination and separation of metals.

Chapter 12 treats of volumetric analysis. The apparatus and solutions employed in volumetric work including a very useful section on indicators.

Chapter 13 gives color methods including an excellent description of the Dubosq colorimeter.

Chapter 14 describes gas analysis. This chapter which is very thorough includes a section on the qualitative determinations of gases, dividing them into groups of combustible and non-combustible, and under each head those that are absorbed and those not absorbed by potassium hydroxide, with tables of the reactions of the different gases under each group. The section on incompatible gases, or those that cannot exist together in a mixture, is very much to the point and is indicative of the thorough way in which M. Carnot treats every portion of his subject.

The publisher's part has been admirably done, the type is large and the pages look beautifully clear, while the cuts which are nearly all line drawings are easily understood.

It is quite impossible to mention all the admirable features of this volume, but what strikes me most forcibly is the clearness and thoroughness which characterize the descriptions of methods and the absolute mastery of detail shown throughout.

ANDREW A. BLAIR.

A TEXT-BOOK OF ELEMENTARY ANALYTICAL CHEMISTRY, QUALITATIVE AND VOLUMETRIC. By J. H. LONG, M.S., Sc.D., Chicago: E. H. Colegrove. 1898. 278 pp. Price $1.50.

The proper presentation of the subject of this book is always difficult, and must vary with the needs of each particular class or instructor. In general, the brief courses of qualitative analysis—the short cuts to a knowledge of the system—are dangerous and tend to loose work on the part of students in that they are led to mechanical performance of the so-called practical methods, rather than to the thoughtful, and thorough

study of the properties and reactions of the elements and compounds, which the methods themselves should serve to illustrate, and upon which they must be based. But the book before us is the sequel to a careful study of the properties of bodies and of the fundamental laws as set forth in the author's excellent work, "Elements of General Chemistry," and therefore in a larger measure free from this objection.

It is divided into two parts, Qualitative Analysis and Volumetric Analysis. In the first part the discussion of the group separations and reactions is preceded by an introduction in which the *raison d' être* for the grouping is briefly but completely and logically set forth, and the illustrative table, presented on page 5, must prove invaluable to the student by offering most comprehensively an exposition of this most important principle of analytical work.

In the discussion of each group we find first the most important and characteristic reactions of the elements constituting it, all well chosen and clearly described; and second the methods for separation of the individual elements of the group. In this latter connection most faithful attention is given to the details to be followed, and precautions to be observed at each step.

The acids are treated in the same manner as the bases and their treatment is followed by two chapters on the systematic analysis of unknown complex substances, brief, but sufficient, constant reference being made to preceding chapters.

The chapter on reactions of a few organic substances, most of the latter having pharmaceutical importance, and that on examination for poisons will find useful application.

In the second part of the work, volumetric analysis is treated in the same logical, thoughtful, painstaking way. The general theory of volumetric methods is clearly set forth and it is fully illustrated in the applications of the principles to the determination of well-known elements. These illustrative methods are followed by special methods which find extensive use, for instance for determination of sugars, starch, glycerol, and for the sanitary analysis of waters.

An appendix giving tabular schemes for the group separations and tests, tables of weights and measures, and tables of solubilities, will be found useful for reference.

The book will be particularly useful in the hands of many instructors who, like Dr. Long, have to do with students who can give but limited time to the study of chemistry and use it merely as auxiliary to the study of other subjects, as medicine, pharmacy, engineering. It is so concise, so complete, so logical in its arrangement, and so clear in the description of the reactions and methods, that our prejudice against the smaller works on these subjects is largely removed, and we are glad to commend it to the careful consideration of those instructors for whom the larger works are too bulky, and who cannot devote to the subject the time these larger works necessarily require.

W. McMURTRIE.

LIGHTING BY ACETYLENE. By WM. E. GIBBS, M. E. New York: D. Van Nostrand Co. 1898. 141 pp. Price $1.50.

This is a popular rather than a scientific exposition of the work which has been done in the effort to make artificial lighting by means of acetylene a practical success. The author in his preface claims that "the safe, efficient, and cheap lighting of houses by acetylene is an accomplished fact," a claim which many doubtless would be ready to dispute.

Short chapters are devoted to the history, dangers, and purification of acetylene; but the bulk of the volume is devoted to descriptions of electric furnaces for the production of the carbide, and generators for effecting its decomposition and the storing of the resulting acetylene gas.

Acetylene lamps and burners claim some twenty pages, and the volume closes with the requirements of the New York fire underwriters, and a list of the U. S. patents relating to this subject. Unfortunately the book has no index.

It is rather surprising to note the amount of brain power which has been devoted to the devising of acetylene generators, and yet the author assures us that "the ideal machine has certainly not yet been invented."

Most gas companies in this country would resent the author's rating of their gas at sixteen candles.

The volume will be found useful by those wishing to try acetylene lighting on a small scale, but we think its value would have been increased if the author had omitted some of the impossible generators and had said something on the details of

installing an acetylene plant, its cost, cost of the light as compared with other artificial illuminants, etc.

The volume is well printed and abundantly illustrated.

E. G. LOVE.

A SHORT COURSE IN INORGANIC QUALITATIVE ANALYSIS FOR ENGINEERING STUDENTS. By J. S. C. WELLS, Instructor in Analytical Chemistry, Columbia University. New York: John Wiley & Sons. 1898. vi + 294 pp.

The author of this book aims, according to the preface, to give a short but thorough course in qualitative analysis for the use of students who have only a limited time to devote to the subject.

This statement, which is frequently repeated in substance in the prefaces to laboratory manuals, and which often denotes a want of completeness in the treatment of the subject, cannot be so understood in the case of the present work.

Beginning with an excellent chapter upon reactions and the use of formulas in general, the author discusses the properties and behavior of bases towards reagents in a thoroughly satisfactory manner. Many chemical facts of general interest are interspersed throughout the book, serving to illustrate the importance of a knowledge of the reactions taught by qualitative analysis.

Equations are used more freely than in some of the larger works and will supply in advance answers to many of a student's questions. The methods directed for use in the separation of the bases of a group are, in the main, those of Fresenius, although modifications are here and there suggested which are undoubtedly to be looked upon as an advance. In his treatment of the separations of acids the author has given some good methods.

In all cases the schemes for separations are presented in the form of tables supplemented by full and detailed explanatory notes. In the part devoted to the analysis of complex mixtures the student receives many useful suggestions. A short chapter upon reagents closes the book.

Altogether, it is quite evident that, in spite of the author's modest limitation of the use of the book to engineering students, it will find a much wider use. The accuracy of treatment and completeness of detail will commend its use both to teacher and student.

F. C. PHILLIPS.

BOOKS RECEIVED.

Crop Circular for September, 1898. United States Department of Agriculture, Washington, D. C. 4 pp.

Bulletin No. 51.—Variations in Milk and Milk Production. 28 pp. Bulletin No. 52.—Orchard Cultivation. 23 pp. Bulletin No. 53.—Abstract—the Chemistry of the Corn Kernel. 4 pp. University of Illinois, Agricultural Experiment Station, Urbana, Ill.

Bulletin No. 76.—Commercial Fertilizers. 9 pp. Bulletin No. 77.—Wheat. 14 pp. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky.

The Fertilizing Value of Street Sweepings. An investigation made under the direction of H. W. Wiley, by Ervin E. Ewell. Bulletin No. 55, U. S. Department of Agriculture, Washington, D. C. 19 pp.

The Apple in North Carolina. A bulletin of practical information for the apple-growers of the state. Bulletin No. 149. The North Carolina Experiment Station, Raleigh, N. C.

Medicinal Plants, which have been collected and used in North Carolina. Bulletin No. 150. 89 pp. The North Carolina Agricultural Experiment Station, Raleigh, N. C.

Zur Erinnerung an R. Fresenius. Seinem verstorbenen Vater in der Zeitschrift für analytische Chemie gewidmeter nachruf von Heinrich Fresenius. Wiesbaden: C. W. Kreidel's Verlag. 1897. 18 pp., with portrait.

Geschichte des chemischen Laboratoriums zu Wiesbaden während der Zweiten 25 Jahre Seine bestehens von Professor Dr. H. Fresenius. Wiesbaden: C. W. Kreidel's Verlag. 1898. 128 pp.

Commercial Organic Analysis. A treatise on the properties, proximate analytical examination, and modes of assaying the various organic chemicals and products employed in the arts, manufactures, medicine, with concise methods for the detection and determination of their impurities, adulterations, and products of decomposition. By Alfred H. Allen, F.I.C., F.C.S. Second Edition. Revised and Enlarged. Volume IV.—Proteids and Albuminous Principles, Proteoïds or Albuminoïds. Philadelphia: P. Blakiston's Son & Co. 1898. 584 pp. Price $4.50.

Essentials of Materia Medica, Therapeutics, and Prescription Writing, arranged in the form of Questions and Answers prepared especially for Students of Medicine. By Henry Morris, M.D. Fifth Edition. Philadelphia: W. B. Saunders. 1898. 288 pp. Price $1.00.

A Text-book of Volumetric Analysis, with Special Reference to the Volumetric Processes of the Pharmacopoeia of the United States, designed for the use of Pharmacists and Pharmaceutical Students. By Henry W. Schimpf, Ph.G., M.D. Third Edition, Revised and Enlarged. New

York: John Wiley & Sons. 1898. xxviii + 522 pp., with fifty-nine illustrations. Price $2.50.

Introduction to Chemical-Technical Analysis. By Prof. F. Ulzer and Dr. A. Fraenkel. Authorized Translation with Appendix by the Translator, Hermann Fleck, Nat. Sc. D. Philadelphia: P. Blakiston's Son & Co. 1898. vii+188 pp. Illustrated. Price $1.25.

Manual of Determinative Mineralogy, with an Introduction on Blowpipe Analysis. By George J. Brush. Revised and Enlarged, with Entirely New Tables for the Determination of Minerals. By Samuel L. Penfield. Fifteenth Edition. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1898. x+312 pp. Price $4.00.

A Manual of Chemical Analysis, Qualitative and Quantitative. By G. S. Newth. New York: Longmans, Green & Co. 1898. xii + 462 pp. Price $1.75.

Soaps. A practical manual of the manufacture of domestic, toilet, and other soaps. By George H. Hunt, F.C.S. Illustrated with 66 engravings. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1898. xii+385 pp. Price $5.00.